

# **TRAINING PROGRAMME FOR TEACHING HARD – SPOTS IN HIGHER SECONDARY CHEMISTRY FOR KRPs OF JAMMU – KASHMIR AND HARYANA STATE.**

**FROM JANUARY 8 – 12, 2004**



**REGIONAL INSTITUTE OF EDUCATION, AJMER-305004  
(National Council of Educational, Research & Training)**

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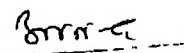


## Foreword

On the recommendation of the Educational Authorities of the states of Jammu and Kashmir and Haryana, Regional Institute of Education, Ajmer undertook an inservice programme for the training of Key Resource Persons (KRPs) in Chemistry at Senior Secondary Level. The Objectives of the programme were a) To prepare instructional material based on new topics included in chemistry syllabus and to train Key Resource Persons in transacting these topics b) performing practicals d) conducting projects and other activities to enhance understanding of the topics

Dr. Sukhvir Singh conducted this programme as programme coordinator. He identified hardspots and newly introduced difficult to teach topics and with his team of Resource Persons including Dr. S C Bhargava, Dr. R.K. Parashar, Mrs. Ruchi Verma and prepared the instructional material and used it for training purpose. The training programme was well conducted.

It is hoped that this programme would help the teacher trainers and teachers to teach chemistry more effectively and efficiently.

  
**Prof. A.B. Saxena**  
**PRINCIPAL**



# PREFACE

At Higher Secondary Level Teaching - Learning process in Chemistry mainly depends upon memorization level, so students find it difficult to cope up with the demands of higher education. National Curriculum Framework for School Education – 2000, gives emphasis on quality of Science Education and teach Chemistry as an elective subject at Senior Secondary stage. NCERT has developed new Textual material in Chemistry in the form of Textbooks in Chemistry for class – XI and XII.

In these new books some new concepts have been added. These new concepts are not easy to transact. In the present training programme these new concepts have been taken as Hard – Spots. Major emphasis has been laid to provide enrichment material on these hard – spots/new topics for dealing these hard –spots. Different strategies of teaching has been adopted. For example how to teach coordination Chemistry through problem – solving method and so on.

Enrichment material provided by the Resource Team was given to the participants. It is hopefully hoped that this will help the Senior Secondary Teachers of Chemistry to develop competencies in transacting the new updated content effectively in the class room and will provide better learning experiences.

In the present five day training programme from January 8 – 12, 2004, seven units have been dealt with viz Coordination Chemistry I and II, Effective nuclear charge, Haloalkanes, Haloarenes, Equilibrium – I/II and Electrochemistry

Besides these theoretical aspects due importance has been given on the activities also. Concept based activities in Chemistry were tried out in the Chemistry Laboratory.

I personally feel grateful for the Academic guidance provided by our worthy Principal, Prof. A. B. Saxena and Prof. H. C. Jain, Head, DESM.

I owe my thanks to the faculty members of chemistry Dr. S. C. Bhargava, Dr. R. K. Parashar and Mrs. Ruchi Verma. I am thankful to our Chemistry Laboratory staff, Sh. Jai Kishan Vats, Sh. Islam Ahmed and Sh. Chhitar Mal. My special thanks are to Sh. Bishamber Dass for the computer typing work.

RIE (NCERT) Ajmer will welcome suggestions from the users of this report.



**(Dr. Sukhvir Singh)**  
**Programme Coordinator**

**Ajmer**  
**January 2004**

# ACKNOWLEDGEMENT

I sincerely acknowledge the Academic guidance and Administrative facilities extended by Prof H. C. Jain, Head, DESM and Prof A B Saxena, Principal, RIE, Ajmer.

I express my thanks to my colleagues Dr. S C. Bhargava, Incharge and Reader in Chemistry, Dr. R. K. Parashar, Lecturer in Chemistry and Mrs. Ruchi Verma, Lecturer in Chemistry for acting as a Resource person in this training programme

My special thanks to all the members of (i) Chemistry Laboratory (ii) Office DESM and (iii) Extension Department for the inputs provided by them during the programme.



**Dr. Sukhvir Singh**  
**Reader in Chemistry**

**January 12, 2004**



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# Coordination Chemistry-I

Dr. Sukhvir Singh

In coordination chemistry sometimes it is customary to write EWENS-BASSET NUMBER in place of stock number. Stock number is oxidation number of metal. It is written in bracket while writing the name of compound. Ewens-Basset Number is formal charge of the complex ion. For example, in  $[\text{Fe}(\text{CN})_6]^{3-}$ , the Ewens Basset Number is -3 and the oxidation number of metal ion is +3. On the basis of this  $\text{K}_3 [\text{Fe}(\text{CN})_6]$  can be given two names. In actual practice stock numbers are generally used. Two names of  $\text{K}_3 [\text{Fe}(\text{CN})_6]$  are:

- i) Potassium hexacyanoferrate (-3)
- ii) Potassium hexacyanoferrate (III)

Other examples are:

$\text{Ba} [\text{BrF}_4]_2$  Barium tetrafluorobromate (-1) and Barium tetrafluorobromate (III)  $\text{Na} [\text{B}(\text{NO}_3)_4]$  Sodium tetranitratoborate (-1) and sodium tetranitratoborate (III).

At present while naming a coordination compound only stock number are used. For various ligands alphabetical order is used. For water acting as a ligand work 'aqua' or 'aquo' can be used.



**Q. 1** Find out the formula of the complex  $\text{CoCl}_3 - 6\text{NH}_3$  if 2.674g of its solution gives 4.305g of AgCl precipitate with  $\text{AgNO}_3$  solution (Molecular mass of  $\text{CoCl}_3 - 6\text{NH}_3 = 267.4$  g and molecular mass of Silver Chloride =  $108 + 35.45 = 143.45$ g).

**Solution:**

143.45g AgCl contains  $\text{Cl}^-$  ions = 35.45g

$$\therefore 4.305 \text{ g AgCl contains } \text{Cl}^- \text{ ions} = \frac{35.45 \times 4.305}{143.4}$$

if  $n$  = number of chloride ions outside the coordination sphere, then 267.4g  $\text{CoCl}_3 - 6\text{NH}_3$  contains  $n \times 35.45$ g of ionizable  $\text{Cl}^-$  ions.

$\therefore$  2.674 of the complex will contain chloride ions  $\frac{n \times 35.45 \times 2.674}{267.4}$  which can be precipitated.

$$\text{Therefore, } \frac{n \times 35.45 \times 2.674}{267.4} = \frac{35.45 \times 4.305}{143.45}$$

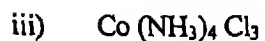
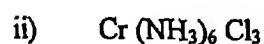
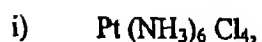
$$\therefore n = \frac{35.45 \times 4.305 \times 267.4}{143.45 \times 35.45 \times 2.674}$$

$$= \frac{4.305 \times 267.4}{143.45 \times 2.674} = 3$$

So number of  $\text{Cl}^-$  ions outside the coordination sphere = Three

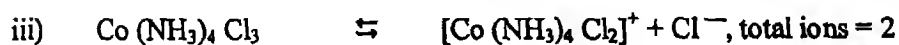
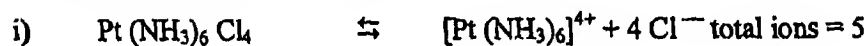
Hence formula of the complex is  $[\text{Co}(\text{NH}_3)_6]^{3+} \text{Cl}_3$

**Q.2** Arrange the following compounds in the increasing order of their conductivity.



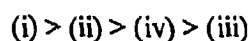
If these are dissolved in water to make its 0.001 M solution.

**Ans.** Molarity data is of no use here for finding out the increasing order of conductivity of the above four compounds. In this case coordination number of the central metal and ionization will be helpful. On the basis of coordination number, ionization of the above compound can be written as:



Conductivity  $\propto$  number of ions

Therefore, order of increasing conductivity is:



**Q .3** Take Nickel Chloride. Add water to make solution. Observe the colour. Add Potassium Cyanide solution. Observe the colour. Explain in detail the coordination chemistry involved in it?

**Ans:** Nickel Chloride salt is soluble in water. Colour will be green due to the formation of complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ . On addition of KCN its green colour disappears due to the formation of complex  $[\text{Ni}(\text{CN})_4]^{2-}$ . Here  $\text{Ni}^{2+}$  is  $d^8$  system. In weak ligand field like  $\text{H}_2\text{O}$ , complex is octahedral and hybridization is  $\text{sp}^3d^2$ , octahedral shape and paramagnetic. In presence of strong ligand field like  $\text{CN}^-$ , electrons in  $3d$  orbitals get paired up leaving a vacant orbital  $dx^2 - y^2$ . This orbital is of high energy. In strong field it is used in bonding, therefore,  $dsp^2$  hybridization will lead to give square planar, diamagnetic, colourless complex ion.

**Q. 4** The magnetic moment of  $[\text{Mn}(\text{CN})_6]^{3-}$  is 2.8 BM and that of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. What are the geometries of these complex ions.

**Ans:**  $[\text{Mn}(\text{CN})_6]^{3-}$  complex is octahedral.

$[\text{MnBr}_4]^{2-}$  is Tetrahedral

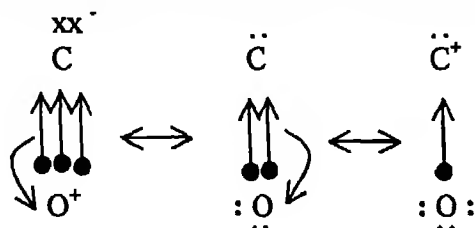
Explanation will be done in the classroom, with active participation from the students.

~~Prepared by~~  
~~Dr. P. S. Choudhary~~

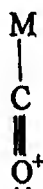
## Coordination Chemistry-II

### Bonding in Metal Carbonyls: -

In carbon monoxide, carbon atom contains lone pair of electrons. This electron pair can be used for the formation of metal-carbon bond in three different ways: -

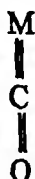


(I) Formation of  $M \leftarrow CO$  bond. In this type of bonding the filled orbital of carbon donates a pair of electrons to the vacant hybrid orbital of the metal forming a  $\sigma$  bond as shown below



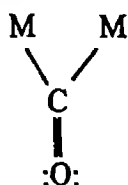
(II) Formation of  $M = CO$  double bond.

In this type of bonding one electron of carbon forms a  $\sigma$  covalent bond with vacant hybrid orbital of the metal atom and another electron of carbon forms a  $\pi$  bond with unhybrid orbital of the metal atom as shown below:



(III) Formation of bonds with two metal atoms: -

In this type of bonding a carbonyl group is attached with two metal atoms as shown below: -

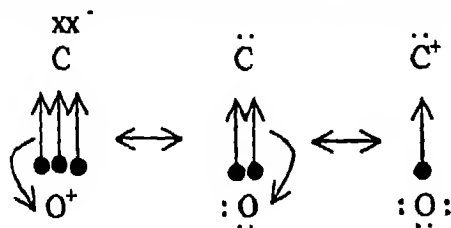


## Coordination Chemistry-II

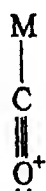
Dr. Sukhvir Singh

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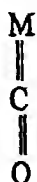


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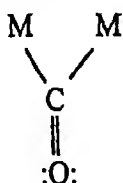
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(III) Formation of bonds with two metal atoms: -

In this type of bonding a carbonyl group is attached with two metal atoms as shown below: -

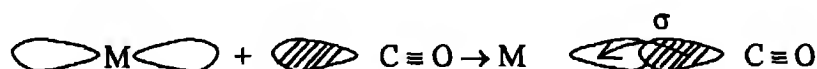


The carbonyl group bonded between two metal atoms is known as bridging carbonyl group. The simplest way of representation is already given in (III) type of bonding. The carbonyl group bonded to a single metal atom is known as Terminal Carbonyl group. This representation is shown in (I) and (II) type of bonding.

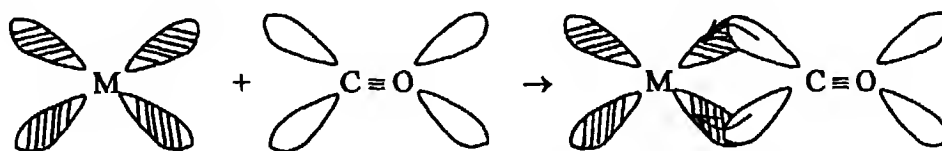
#### Sigma and Pi bonding in metal carbonyls: -

Diagrammatic representation of  $\sigma$  and  $\pi$  bonding in metal carbonyls is self explanatory as given below: -

##### Diagram of $\sigma$ bonding: -



##### Diagram of $\pi$ bonding: -



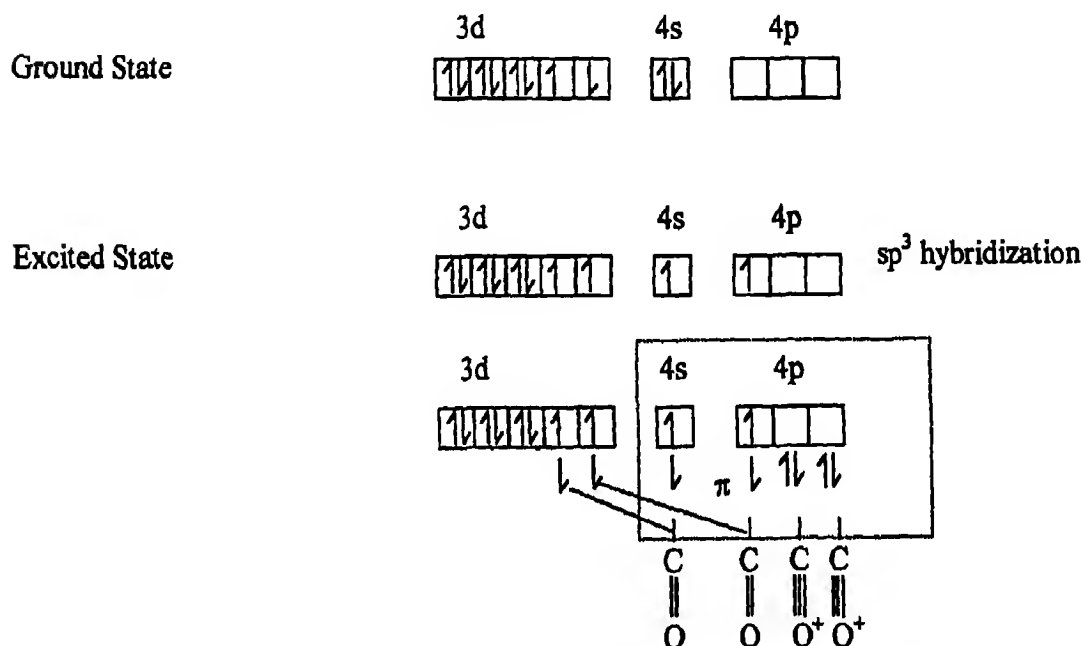
The filled orbital of carbon atom of carbonyl group donates an electron pair to the vacant hybrid orbital of the metal atom and forms a coordinate bond  $\sigma$ . The filled d orbital of the metal atom overlaps with vacant anti-bonding p-orbitals of carbon atom to form a  $d\pi - p\pi^*$  bond. The stronger  $\sigma$  bonding causes the  $\pi$  electrons shift to a greater extent from metal to carbon. Similarly,  $\pi$ - bonding increases electron density on carbon atom and makes it to transfer more electrons on metal through  $\sigma$  bonding. In other words  $\sigma$  bonding strengthens  $\pi$  bonding and  $\pi$  bonding strengthens  $\sigma$  bonding. Such mechanism is known as synergic mechanism.

Metal carbon bonding can be made clearer by giving suitable examples upto the level of Sr. Secondary stage.

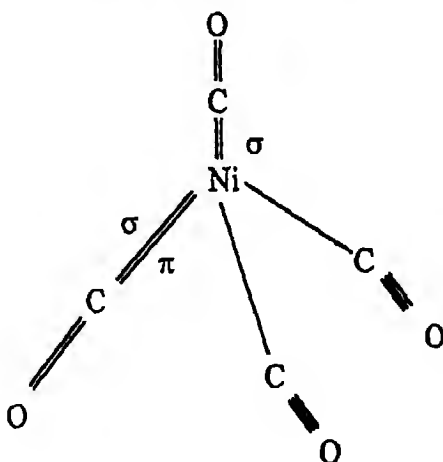
**Example -I: Nickel Tetra Carbonyl, Ni (CO)<sub>4</sub>**

Nickel atom in Ni (CO)<sub>4</sub> is tetrahedrally hybridized (sp<sup>3</sup>). Out of four sp<sup>3</sup> hybrid orbitals of nickel two are vacant and two are half filled. Two carbonyl groups donate their electron pair to two vacant sp<sup>3</sup> hybrid orbitals of nickel atom forming two M-C, σ bonds. Remaining two CO groups form σ bonds with half filled sp<sup>3</sup> hybrid orbitals and π-bonds with half filled d-orbitals. Orbital diagram of Ni (CO)<sub>4</sub> is given below: -

Ni [28]: 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 3d<sup>8</sup>, 4s<sup>2</sup>

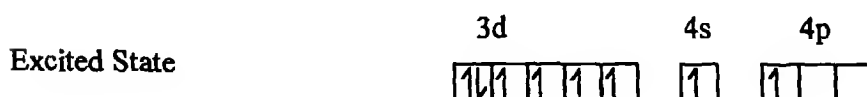
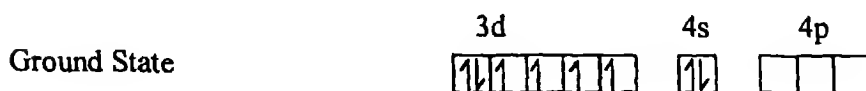
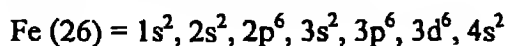


Thus in Ni (CO)<sub>4</sub> two CO groups are bonded through single bonds and two with double bonds to the nickel atom. The molecule is tetrahedral.

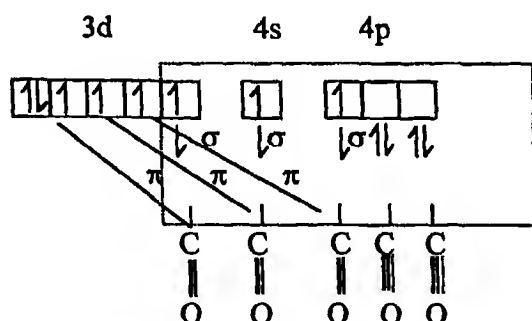


## Example 2: - Iron Pentacarbonyl, $\text{Fe}(\text{CO})_5$

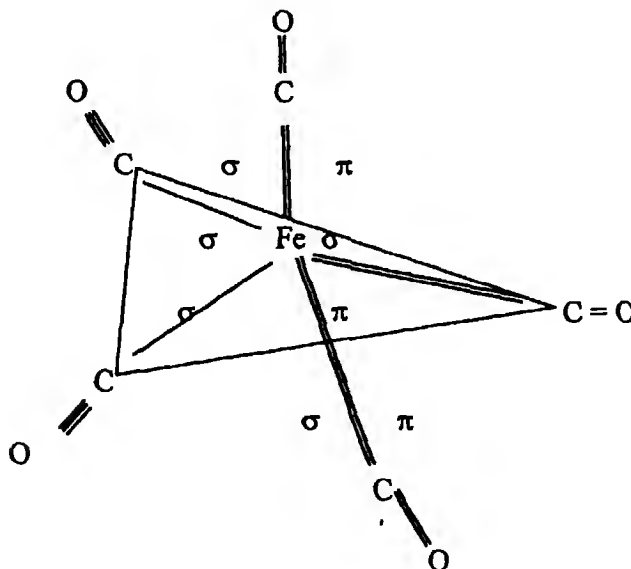
Iron atom in  $\text{Fe}(\text{CO})_5$  is  $\text{dsp}^3$  hybridized. It has two vacant hybrid orbitals and three half filled hybrid orbitals. Two of the CO groups are bonded by coordinate bonds and the remaining three CO groups form double bond with the metal atom. Orbital diagram of  $\text{Fe}(\text{CO})_5$  is given below:



The geometry of the molecule is Trigonal bipyramidal

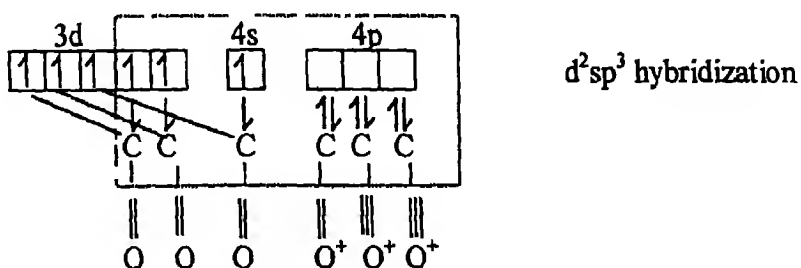
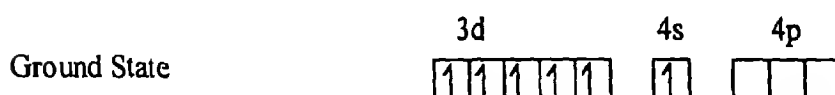
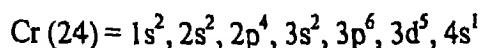


Thus in  $\text{Fe}(\text{CO})_5$  two CO groups are of different nature and three are of different nature. Therefore, single bond can be replaced easily.  
 $\text{dSP}_3$  Hybridization.

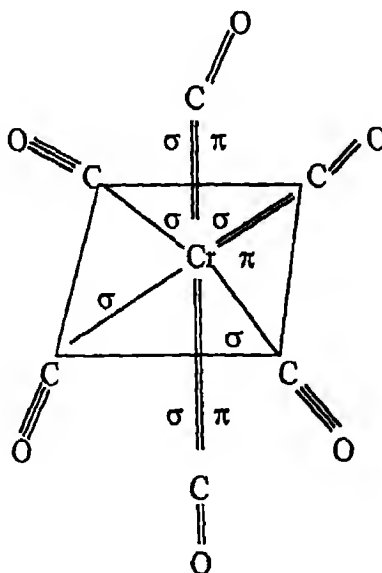


**Example 3: Chromium hexacarbonyl,  $\text{Cr}(\text{CO})_6$**

Chromium atom in  $\text{Cr}(\text{CO})_6$  is in  $d^2sp^3$  hybrid state. It has three vacant and three singly occupied hybrid orbitals. Three empty orbitals form coordinate bond with three CO groups. The other CO groups form double bond with metal. Orbital diagram is shown below:



In  $\text{Cr}(\text{CO})_6$ , three of the CO groups would be different from the other three. The molecule is octahedral in shape



**Assignment:** - find out effective atomic number in  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ .

- 2) Magnetic property of sodium nitro prusside.
- 3) Magnetic property of Ferrocene.

## : TRANSITION ELEMENTS

### 3.0 INTRODUCTION

Before starting transition elements let us make clear the concept of effective nuclear charge.

#### 3.1 EFFECTIVE NUCLEAR CHARGE

The most stable electronic state within a degenerate set of orbitals is the state having maximum spin multiplicity. That is the one with the largest number of unpaired electron spins. It means that electrons spread out into the space as much as possible around the nucleus. Hund's rule also implies that this spreading out of electron density leads to extra stability not only for the individual electron at hand but also for the rest of electrons. It is important to understand how this stability arises. Part of the explanation involves the concept of effective nuclear charge.

We know that an electron will occupy that orbital (vacant) on an atom where the nucleus is most effective at offering positive charge to stabilise the electron. It was J.C. Slater who realized that the effective nuclear charge  $Z^*$  which is felt by an electron is not the actual charge  $Z$  of the nucleus of the atom. The amount of nuclear charge actually felt by an electron depends on the type of orbital in which the electron is placed and on the ability of other electrons in more penetrating orbitals to shield (or screen) the electron in

question from the nucleus.

For the orbitals having the same value of principal quantum number ( $n$ ), the s orbital is the most stable.

The order of penetration of electron cloud of other orbitals is  $s > p > d > f$  and so on. Thus for any principal quantum number ' $n$ ', an electron will experience the greatest effective nuclear charge when placed in an s orbital then a p orbital and so on. It was cited as the reason for the order of orbital filling among the elements. But what of the atoms of the p-block of the periodic table where the last electron is placed in every case into an orbital of the same type. Second row of the periodic table begins with B and ends at Ne. From B to Ne each new electron is added in accordance with Hund's rule. Also each new electron experiences a new and different effective nuclear charge. At B the new electron is added into one of the p-orbitals say the  $p_x$  orbital. The new electron that is added for C must now go into another of the 2p orbital say  $p_y$ .  $p_y \perp p_x$  orbital is poorly shielded from the nuclear charge by the  $p_x$  orbital. Therefore, the effective nuclear charge for the last electron in C is higher than that for B. It is the geometry and the orientation of the p-orbital, that makes them poor at shielding one another from the nucleus. Consider the next element N. The third p electron that is added to make this

element is poorly screened from the growing nuclear charge because the other two p electrons that are already there lie at  $90^\circ$  to this last one. Thus the effective nuclear charge for the differentiating electron of nitrogen is even higher when screening of an electron is poor, the effective nuclear charge is high. Thus Hund's rule is followed. That is electrons spread out into a degenerate set of orbitals in order to experience this maximum effective nuclear charge. Besides this simple view there are other factors also like Quantum Mechanical Exchange Energy with a set of electrons with parallel spin that influence the energies of the various electron configurations.

J.C. Slater proposed an empirical constant that represents the cumulative extent to which the other electrons of an atom shield (or screen) any particular electron from the nuclear charge. Therefore, Slater's screening constant  $\sigma$  is used.

$$Z^* = Z - \sigma$$

$Z$  = At. number of the atom and hence is equal to the actual number of protons in the atom. The parameter  $Z^*$  is the effective nuclear charge which according to above eqn. is smaller than  $Z$  since the electron in question is screened (shielded) from  $Z$  by an amount  $\sigma$ . Trend for  $Z^*$  becomes difficult for subsequent rows. However  $Z^*$  increases from left to right across a period.

## CALCULATION OF $Z^*$

The value of  $\sigma$  for any one electron in a given electronic configuration (i.e. in the presence of the other electrons of the atom in question) is calculated using a set of rules developed by Slater. According to these rules the value of  $\sigma$  for the electron in question is the cumulative total provided by the various other electrons of the atom. The other electrons of the atom each add an intrinsically different contribution to the value of  $\sigma$  as follows:

### WHEN THE ELECTRON IN QUESTION <sup>is</sup> BESIDES IN AN S OR p ORBITAL

- 1 All electrons in principal shells higher than the electron in question contribute zero to  $\sigma$ .
- 2 Each electron in the same principal shell contribute 0.35 to  $\sigma$ .
- 3 Electrons in the (n-1) shell each contribute 0.85 to  $\sigma$ .
- 4 Electrons in deeper shells each contribute 1.00 to  $\sigma$ .

### WHEN THE ELECTRON IN QUESTION <sup>is</sup> BESIDES IN A d or f ORBITAL

- 1 All electrons in principal shells higher than the electron in question contributes zero to  $\sigma$ .
- 2 Each electron in the same principal shell contributes 0.35 to  $\sigma$ .

- 3 All inner-shell electrons i.e. (n-1) and lower uniformly contributes 1.00 to  $\sigma$ .

CALCULATION OF  $Z^*$  FOR FIRST AND SECOND ROW OF THE PERIODIC

TABLE:

First Row:

1. Hydrogen Symbol = H Atomic number = 1

Electronic configuration  $1s^1$ ,  $\sigma = 0$

$$Z = 1, \quad \sigma = 0$$

$$Z^* = Z - \sigma = 1 - 0 = 1 \text{ Ans.}$$

2. Helium, Symbol = He, Atomic number = 2

Electronic configuration =  $1s^2$

$$Z = 2, \quad \sigma = 1 \times 0.35 = 0.35$$

$$Z^* = Z - \sigma = 2.0 - 0.35 = 1.65 \text{ Ans.}$$

SECOND ROW:

1. Lithium, Symbol = Li, atomic number = 3

Electronic configuration =  $1s^2 2s^1$

$$Z = 3$$

$$\sigma = 2 \times 0.85 + 0 = 1.70$$

$$Z^* = Z - \sigma = 3.0 - 1.7 = 1.3 \text{ Ans.}$$

2. Beryllium, symbol = Be, Atomic number = 4

Electronic configuration =  $1s^2 2s^2$

$$Z = 4$$

$$\sigma = 2 \times 0.85 + 1 \times 0.35 = 1.70 + 0.35 = 2.05$$

$$Z^* = 4 - 2.05 = 1.95 \text{ Ans.}$$

3. Boron, Symbol = B, Atomic number = 5

Electronic configuration =  $1s^2 2s^2 2p^1$

$$Z = 5$$



$$\sigma = 2 \times 0.85 + 2 \times 0.35 = 1.70 + 0.70 = 2.40$$

$$Z^* = 5 - 2.4 = 2.6 \text{ Ans.}$$

iv) Carbon, symbol = C, atomic number 6

Electronic configuration =  $1s^2 2s^2 2p^2$

$$Z = 6$$

$$\sigma = 2 \times 0.85 + 3 \times 0.35 = 1.70 + 1.05 = 2.75$$

$$Z^* = 6.0 - 2.75 = 3.25 \text{ Ans.}$$

v) Nitrogen, symbol = N, atomic number = 7

Electronic configuration =  $1s^2 2s^2 2p^3$

$$Z = 7$$

$$\sigma = 2 \times 0.85 + 4 \times 0.35 = 1.70 + 1.40 = 3.10$$

$$Z^* = 7.0 - 3.1 = 3.90 \text{ Ans.}$$

vi) Oxygen, Symbol = O, atomic number = 8

Electronic configuration =  $1s^2 2s^2 2p^4$

$$Z = 8,$$

$$\sigma = 2 \times 0.85 + 5 \times 0.35 = 1.70 + 1.75 = 3.45$$

$$Z^* = 8.0 - 3.45 = 4.55 \text{ Ans.}$$

vii) Fluorine, Symbol = F, Atomic number = 9

Electronic configuration =  $1s^2 2s^2 2p^5$

$$Z = 9.00, \sigma = 2 \times 0.85 + 6 \times 0.35 = 3.80$$

$$Z^* = 9.00 - 3.80 = 5.20 \text{ Ans.}$$

viii) Neon, Symbol = Ne, Atomic number = 10

Electronic configuration =  $1s^2 2s^2 2p^6$

$$Z = 10$$

$$\sigma = 2 \times 0.85 + 7 \times 0.35 = 1.70 + 2.45 = 4.15$$

$$Z^* = 10.00 - 4.15 = 5.85 \text{ Ans.}$$

ix) Sodium symbol Na atomic number = 11  
 Electronic configuration =  $1s^2 2s^2 2p^6 3s^1$   
 $Z=11$

$$\sigma = 2 \times 1.0 + 8 \times 0.85 + 0 \times 0.35$$

$$= 2.0 + 6.80 = 8.80$$

$$Z^* = Z - \sigma = 11 - 8.8 = 2.20$$

x) Magnesium symbol = Mg, At.No.12

Electronic configuration =  $1s^2 2s^2 2p^6 3s^2$

$$Z = 12$$

$$\sigma = 2 \times 1.0 + 8 \times 0.85 + 1 \times 0.35$$

$$= 2.0 + 6.8 + 0.35$$

$$= 9.15$$

$$Z^* = 12 - 9.15 = 2.85$$

# HALOALKANES, HALOARENES

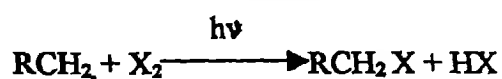
Dr. R.K. Parashar

## HALOALKANES

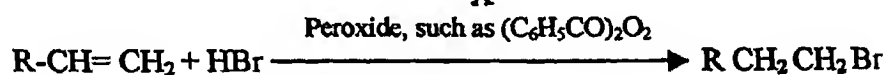
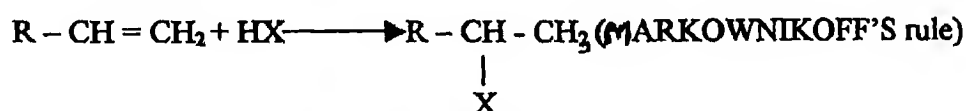
Halogen derivatives of saturated hydrocarbons are called haloalkanes (also known as alkylhalides) General formula of haloalkanes is  $RX$  where  $R$  is an alkyl group ( $C_nH_{2n+1}$ ) and  $X$  is a halogen atom

(F, Cl, Br or I)

### 1 Direct Halogenation of Alkane



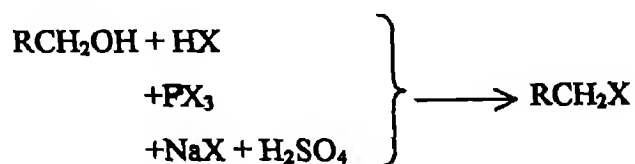
### 2 Addition of HX to alkenes



(Anti Markownikoff addition)

(Peroxide effect does not apply to the addition of HCl and HI)

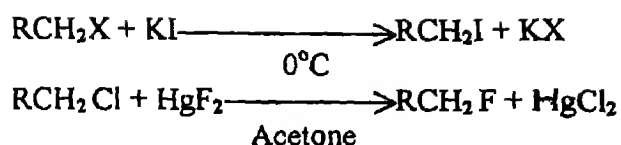
### 3. Replacement of - OH in R - OH (Alcohols)



Comments.

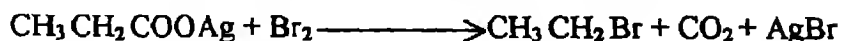
- Order of reactivity of HX is  $HI > HBr > HCl$
- Order of reactivity of ROH is Tertiary > Sec > Primary

#### 4 Halogen Exchange



#### 5 Hunsdiecker Reaction

Silver salt of Carboxylic acid is treated with  $\text{Br}_2$  in  $\text{CCl}_4$



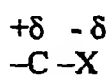
- This method is used to get rid of a C-atom

#### Characteristics of Haloalkanes

- Physical characteristics are influenced by the polar nature of R-X bond
- Haloalkanes are insoluble in water as they cannot form H – bonds with water.
- Boiling points of Haloalkanes are higher than corresponding alkanes, due to polar nature of alkyl halides and consequent stronger dipole – dipole attractions.
- Boiling points increase in the order  $\text{R} - \text{Cl} < \text{R} - \text{Br} < \text{R} - \text{I}$  due to increased van der Waals attractions.
- For the same halogen atom the boiling points increase with increase in size of R group.
- For isomeric compounds the boiling point is less for branched chain isomer. Branched chain isomers have smaller surface area and weaker van der Waals forces of attraction.

#### Chemical Properties

Because of high electronegativity of the halogen atom, the carbon halogen (C-X) bond is highly polarized covalent bond



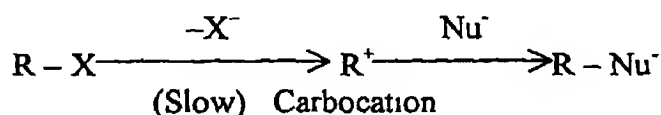
Thus the carbon atom of the C – X bond becomes a good site for attack by electron rich species (nucleophiles or nucleophilic reagents) In fact nucleophilic substitution (replacement of the halide ion by a nucleophile) reactions are the most common reactions of alkyl halides



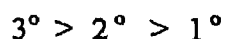
The common nucleophiles are  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{SH}^-$ ,  $\text{NH}_2^-$ ,  $\text{OR}^-$  and  $\text{RCOO}^-$

Nucleophilic substitution may take place in two ways

### 1 $\text{S}_\text{N}^1$ Mechanism (Unimolecular nucleophilic substitution)

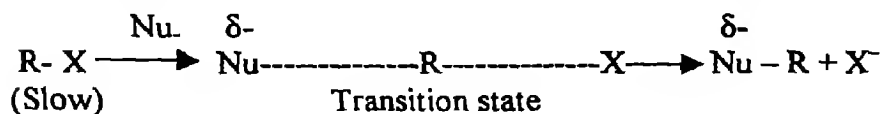


The tertiary alkyl halides react by  $\text{S}_\text{N}^1$  mechanism via formation of carbocation intermediate. The reactivity order for  $\text{S}_\text{N}^1$  reaction is

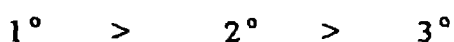


Remember that in case alkyl halide is optically active,  $\text{S}_\text{N}^1$  reactions lead to racemisation

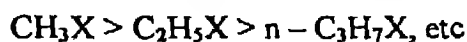
### 2 $\text{S}_\text{N}^2$ Mechanism (Bimolecular nucleophilic substitution)



Primary alkyl halides undergo hydrolysis by  $\text{S}_\text{N}^2$  mechanism via formation of a transition state. The reactivity order of  $\text{S}_\text{N}^2$  reaction is



The order of reactivity among various  $1^\circ$  alkyl halides is

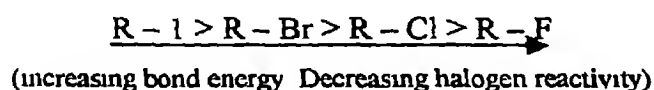


Bulkier the alkyl group, more is the steric hindrance in the formation of transition state and less is the reactivity of alkyl halide (remember that it is contrary to the stability of the carbonium ion  $n\text{-C}_3\text{H}_7^+ > \text{C}_2\text{H}_5^+ > \text{CH}_3^+$ , but here carbonium ion is not formed as an intermediate)

Remember that in case alkyl halide is optically active,  $\text{SN}^2$  reactions lead to Walden inversion

In short,  $3^\circ$  alkyl halides react by  $\text{SN}^1$ ,  $1^\circ$  by  $\text{SN}^2$  and  $2^\circ$  by either or both of these mechanism depending upon the nature of the alkyl halide and the reagent

For a given alkyl group, the order of reactivity is



This is in accordance with the carbon-halogen bond energy, the carbon-fluorine bond energy is maximum and thus fluorides are the least reactive while carbon-iodine bond energy is minimum and hence iodides are the most reactive.

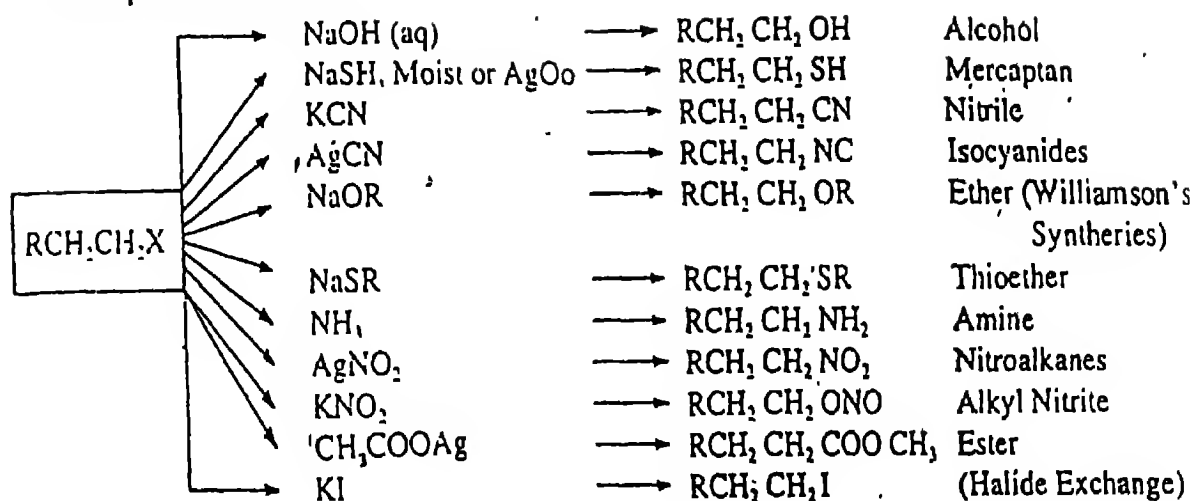
In addition to substitution reactions, alkyl halides also undergo elimination reactions to form alkenes with the removal of a molecule of hydrogen halide (dehydrohalogenation) In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as  $\beta$  - elimination may proceed by  $\text{E}^1$  or  $\text{E}^2$  mechanism (analogous to  $\text{SN}^1$  and  $\text{SN}^2$  mechanism) The order of elimination reaction is



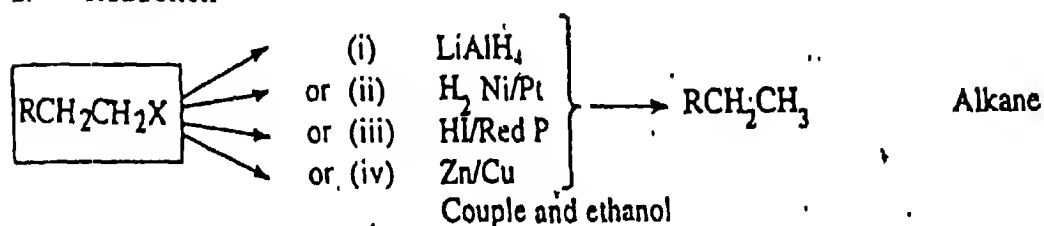
In general  $3^\circ$  halides lead to react by elimination,  $1^\circ$  halides by substitution and  $2^\circ$  halides by either or both of the reactions

In short alkyl halides can be converted into nearly all the types of organic compounds and thus provide important synthetic tool in the hands of an organic chemist

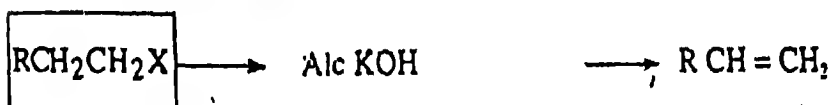
## I. Nucleophilic substitution



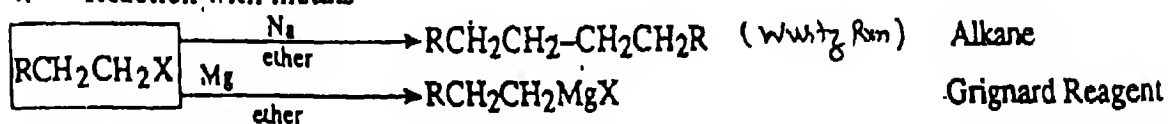
## 2. Reduction



## 3. Elimination reactions



## 4. Reaction with metals

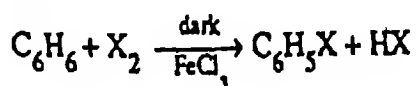


## HALOARENES

Halogen derivatives of aromatic Hydrocarbons are called haloarenes (or aryl halides). General formula is  $\text{Ar-X}$ .

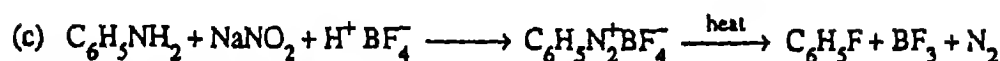
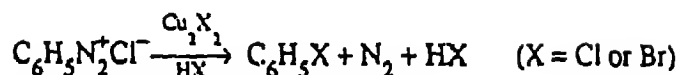
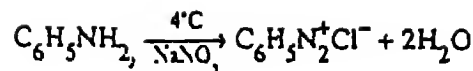
### Preparation of Haloarenes

#### 1. Direct halogenation of arenes



## 2. From Diazonium Salts

### (a) Sandmeyer's Reaction

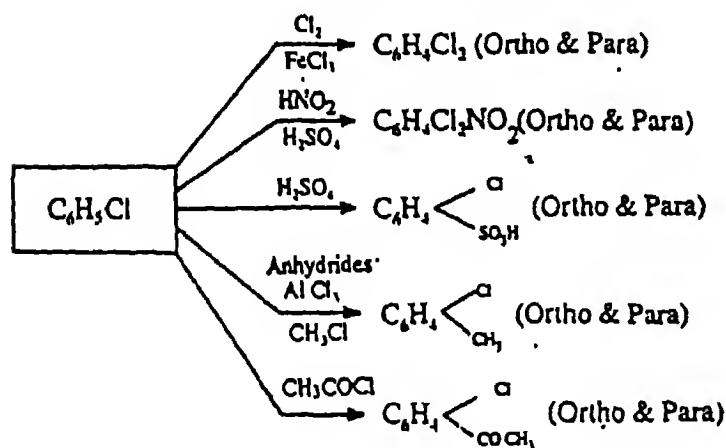


### Characteristics of Haloarenes.

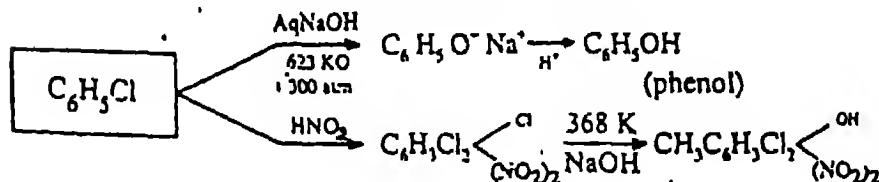
- Haloarenes are more stable and less reactive than haloalkanes due to the following :
  - (a) In haloarenes the carbon atom in the C — X bond is  $sp^2$  hybridised and is thus more electronegative than the  $sp^3$  hybridised carbon atom of alkyl halides C — X bond in haloalkanes is thus less polar.
  - (b) The C — X bond in haloarenes is shorter than C — X bond in haloalkanes (C in R — X is  $sp^3$  hybridised while C in Ar — X is  $sp^2$  hybridised).
- Boiling points generally follow the same order as haloalkanes. Melting points of para-isomer are different due to symmetrical structure and close packing of such molecules in a crystal lattice.
- Haloarenes undergo electrophilic substitution at ortho and para positions.
- Nucleophilic substitution is difficult and takes place under drastic conditions.

### Summary of Reactions of Haloarenes

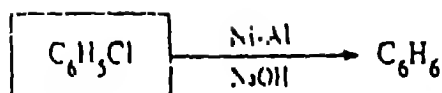
#### 1. Electrophilic Substitution (Ring Substitution)



#### 2. Nucleophilic Substitution



### 3. Reduction



### 4. Wurtz-Fittig Reaction



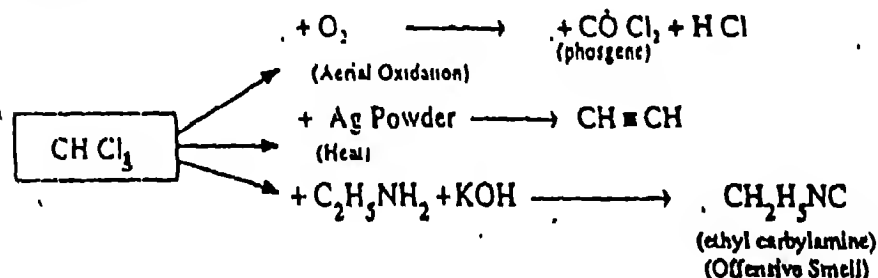
## POLY-HALIDES

### Chloroform ( $\text{CHCl}_3$ )

Obtained by direct chlorination of methane or by the action of bleaching powder ( $\text{CaOCl}_2$ ) on ethanol or acetone (Haloform reaction)

Sweet smelling liquid insoluble in water; slowly oxidised in air to  $\text{COCl}_2$  (phosgene). Hence stored in coloured bottles

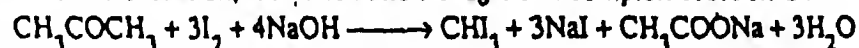
#### Reactions



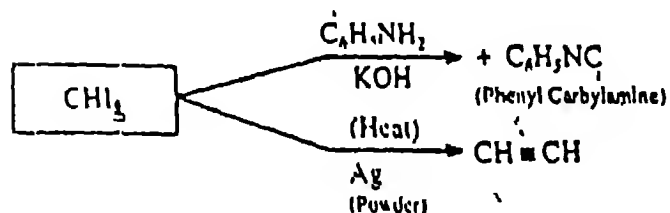
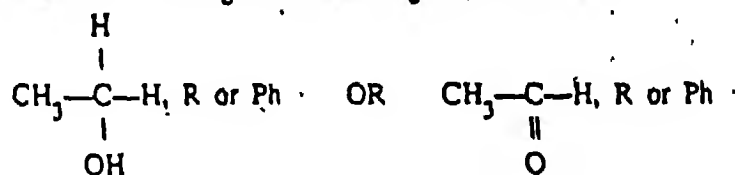
### Iodoform ( $\text{CHI}_3$ )

Obtained from acetone or ethanol by treating with  $\text{I}_2$  and  $\text{NaOH}$  (Iodoform test)

The reaction involves oxidation, iodination and cleavage. The complete reaction is:



Compounds that contain the following structural unit give the Iodoform test



Freon — ( $\text{CCl}_2\text{F}_2$ ) used as a refrigerant

DDT — 2, 2-bis (p-chlorophenyl) 1, 1, 1-trichloro-ethane used as an insecticide.

BHC —  $\text{C}_6\text{H}_6\text{Cl}_6$  (Benzene hexachloride) gamma-xylene or lindane is an insecticide.



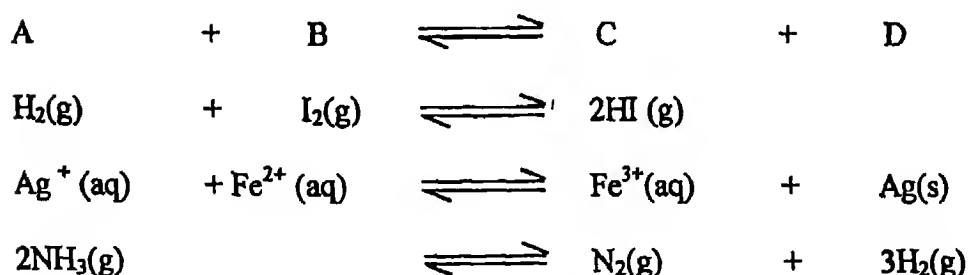
# EQUILIBRIUM – I

Dr. R.K. Parashar

## 1. INTRODUCTION

It is an experimental fact that most of the processes including chemical reactions, when carried out in a closed vessel, do not go to completion. Under these conditions, a process starts by itself or by initiation, continues for some time at diminishing rate and ultimately appears to stop. The reactants may still be present but they do not appear to change into products any more.

A reaction is said to be reversible if the composition of reaction mixture on the approach of equilibrium at a given temperature is the same irrespective of the initial state of the system, i.e. irrespective of the fact whether we start with reactants or the products. Some examples are:



## CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

- The equilibrium is dynamic i.e. the reaction continues in both forward and reverse direction.
- The rate of forward reaction equals the rate of reverse reaction.
- The observable properties of the system such as pressure, concentration, density remain invariant with time.
- The chemical equilibrium can be approached from either side.

A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.

**Law of mass action:** Guldberg and Waage proposed that "The rate at which a substance reacts is directly proportional to its active mass and rate of a chemical reaction is directly proportional to product of active masses of reactants each raised to a power equal to corresponding stoichiometric coefficient appearing in the balanced chemical equation".

For dilute solutions active mass is equal to concentration. Taking the example of the reaction.



We can write,

Rate of forward reaction  $r_f \propto [\text{N}_2] [\text{H}_2]^3$  rate of reverse reaction  $r_r \propto [\text{NH}_3]^2$

## 2. EQUILIBRIUM CONSTANTS ( $K_p$ & $K_c$ ):

Consider the reaction:



The rate of forward reaction =  $k_f[\text{A}][\text{B}]$

The rate of reverse reaction =  $k_r[\text{C}][\text{D}]$

At equilibrium, the two rates are equal.

$$\therefore k_f[\text{A}][\text{B}] = k_r[\text{C}][\text{D}]$$

$$\therefore \frac{k_f}{k_r} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

$$\therefore \frac{k_f}{k_r} \text{ is called equilibrium constant } K$$

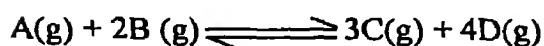
The concentrations of A(s) is a constant (d/M). Therefore for the above equilibrium not only is  $\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$  a constant but  $\frac{[\text{C}][\text{D}]}{[\text{B}]}$  is also a constant which is equal  $K \times [\text{A}]$ .  $\frac{[\text{C}][\text{D}]}{[\text{B}]}$

$$\therefore K[\text{A}] \frac{[\text{C}][\text{D}]}{[\text{B}]} = \text{constant}$$

This constant is called  $K_C$

This constant between  $K_C$  and  $K$  is that in the expression of  $K$  all the substances are involved and in the expression of  $K_C$  only solutions and gases are involved. the expression of  $K_C$  is devoid of any constants, i.e., solids and pure liquids.

Now consider the reaction:



$$K_C = K = \frac{[C]^3 [D]^4}{[A] [B]^2}$$

Since for a gas  $PV = nRT$ ,  $P = \frac{n}{V} RT$ ,

$$\therefore \frac{n}{V} = \frac{P}{RT} \quad \therefore [C] = \frac{P_C}{RT} \quad [D] = \frac{P_D}{RT}$$

$$[A] = \frac{P_A}{RT} \text{ and } [B] = \frac{P_B}{RT}$$

$$K_C = \frac{\left(\frac{P_C}{RT}\right)^3 \left(\frac{P_D}{RT}\right)^4}{\left(\frac{P_A}{RT}\right)^1 \left(\frac{P_B}{RT}\right)^2} = \frac{P_C^3 P_D^4}{P_A P_B^2} \times \frac{(RT)^1 \times (RT)^2}{(RT)^3 \times (RT)^4}$$

$$K_C (RT)^{(3+4)-(2+1)} = \frac{P_C^3 P_D^4}{P_A P_B^2}$$

Since  $K_C$  is a constant,  $RT$  is a constant, It implies that for this equilibrium the ratio of the partial pressures (each raised to the proper powers) is also a constant. This ratio is called  $K_p$

$\therefore K_p = K_C (RT)^{\Delta n}$  where  $\Delta n = \text{Total moles of product gases} - \text{Total moles of reactant gases}$ .

$$K_p = \frac{P_C^3 P_D^4}{P_A P_B^2}$$

It is important to understand that in the above reaction if anyone of the components were a solid or a pure liquid, the only change that we can have in the expression of  $K_p$  is the absence of that component: For example, If A were a solid or a pure liquid, its concentration would be a constant

$$\therefore K_c = \frac{[C]^3[D]^4}{[B]^2} \text{ and therefore } K_p = \frac{P_C^3 P_D^4}{P_B^2}$$

This happens because [A] will not figure in the expression of  $K_c$  itself.

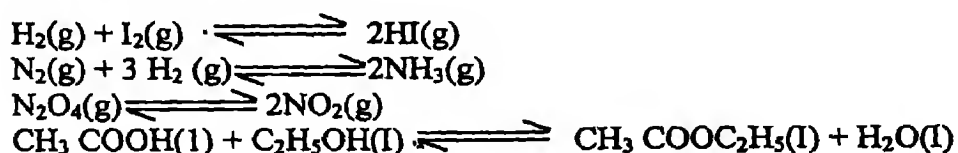
But if A were a solution, its concentration would be there in the expression of  $K_c$ . Since the concentration of a solution is not  $\frac{P}{RT}$  as it is for a gas we can see that the expression of  $K_p$  is not derivable

$\therefore K_p$  does not exist for an equilibrium which has anyone component as a solution.

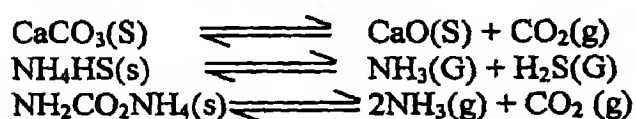
### Types of Equilibria

There are mainly two types of equilibria:

- a) **Homogeneous:** Equilibrium is said to be homogeneous if reactants and products are in same phase.

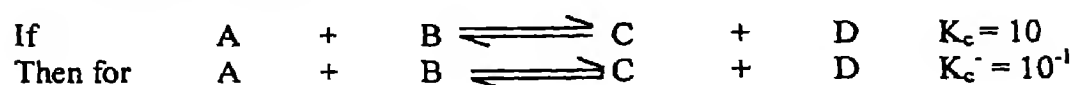


- b) **Heterogeneous:** Equilibrium is said to be heterogeneous if reactants and products are in different phases

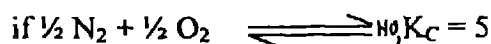


### IMPORTANT RELATIONSHIPS INVOLVING EQUILIBRIUM CONSTANT:

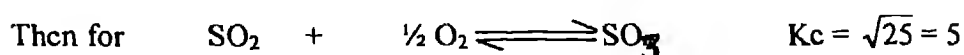
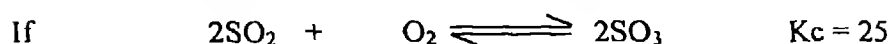
If we reverse an equation,  $K_c$  or  $K_p$  is inverted i.e.



If we multiply each of the coefficient in a balanced equation by a factor n, then equilibrium constant is raised to the same factor.



If we divide each of the coefficients in a balanced equation by the factor n, then new equilibrium constant is nth root of the previous value



When we combine individual equation we have to multiply their equilibrium constants for reaction if  $K_1$ ,  $K_2$  and  $K_3$  are stepwise equilibrium constant for  $A \rightleftharpoons B$ ,  $B \rightleftharpoons C$ ,  $C \rightleftharpoons D$ , Then for  $A \rightleftharpoons D$ , equilibrium constant is  $K = K_1 \cdot K_2 \cdot K_3$

#### Significance of the Magnitude of on Equilibrium Constant:

- A very large value of  $K_c$  or  $K_p$  signifies that the forward reaction goes to completion or very nearly so.
- A very small value of  $K_c$  or  $K_p$  signifies that the forward reaction does not occur to any significant extent.
- A reaction is most likely to reach a state of equilibrium in which both reactants and products are present if the numerical value of  $K_c$  or  $K_p$  is neither very large nor very small.

### 3 RELATIONSHIP BETWEEN $\Delta G^\circ$ AND K

Free energy, G, denotes that self intrinsic electrostatic potential energy of a system. This means that in any molecule if we calculate the total electrostatic potential energy of all the charges due to all the other charges, we get what is called the free energy of the molecule. It tells about the stability of a molecule with respect to another molecule. Lesser the free energy of a molecule more stable it is.

Every reaction proceeds with a decrease in free energy. The free energy change in a process is expressed by  $\Delta G$ . If it is negative, it means that

products have lesser G than reactants, so the reaction forward. If it is positive the reaction goes reverse and if it is zero the reaction is at equilibrium

$\Delta G$  is the free energy change at any given concentration of reactants and products. If all the reactants and products are taken at a concentration of 1 mole per liter, the free energy change of the reaction is called  $\Delta G^\circ$  (Standard free energy change).

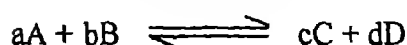
One must understand that  $\Delta G^\circ$  is not the free energy change at equilibrium. It is the free energy change when all the reactants and products are at a concentration of 1 mole/L.  $\Delta G^\circ$  is related to K (equilibrium constant) by the relation,  $\Delta G^\circ = -RT \ln K$ . K may either be  $K_c$  or  $K_p$ . Accordingly we get  $\Delta G_p^\circ$ .

~~The value of  $\Delta G^\circ$  depends only on Room Temperature, Temperature, Concentration in Kc, and  $\Delta G^\circ$  is in J/mol, and  $\Delta G_p^\circ$  is in calories, and  $\Delta G^\circ$  will be in calories.~~

### Reaction Quotient (Q)

At each point in a reaction, we want<sup>to</sup> formulate a ratio of concentration terms ~~using the same~~ for ~~the~~ the equilibrium constant expression. This ratio is called the reaction quotient denoted as symbol Q. It helps in predicting the direction of a reaction.

### FOR A GENERAL REACTION



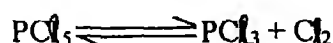
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- If the reaction is at equilibrium,  $Q = K_c$
- A net reaction proceeds from left to right (forward direction) if  $Q < K_c$
- A net reaction proceeds from right to left (the reverse direction) if  $Q > K_c$

## 4. LE CHATLIER'S PRINCIPLE

This is based on the fundamental of a stable equilibrium. It states that “when a system at equilibrium is subjected to a change in temperature, pressure or concentration of a reacting species The system reacts in a way that partially offsets the change while reaching a new state of equilibrium”

This can be understood by the following example. Overall we can also predict the direction of equilibrium by keeping in mind following theoretical assumption



Let us assume that we have this reaction at equilibrium and the moles of  $\text{Cl}_2$ ,  $\text{PCl}_3$  and  $\text{PCl}_5$  at equilibrium are a, b and c respectively, and the total pressure by  $P_T$

$$\therefore K_p = \frac{\left( \frac{a}{a+b+c} \times P_T \right) \left( \frac{b}{a+b+c} \times P_T \right)}{\left( \frac{c}{a+b+c} \times P_T \right)} = \frac{abP_T}{c(a+b+c)}$$

$$\text{Since } P_T = \frac{(a+b+c)RT}{V}$$

$$\therefore K_p = \frac{abRT}{cV}$$

Now if d moles of  $\text{PCl}_3$  is added to the system the value of Q would be,  $\frac{a(b+d)RT}{cV}$   
we can see that this is more than  $K_p$ . So the system would move reverse to attain equilibrium.

- If we increase the volume of the system, the Q becomes  $\frac{abRT}{cV'}$  Where  $V' > V$ .  $\therefore$  Q becomes less, and the system would move forward to attain equilibrium.
- If we add a noble gas at constant pressure, it amounts to increasing the volume of the system and therefore the reaction moves forward

- If we add the noble gas at constant volume, the expression of  $Q$  remains as  $Q = \frac{abRT}{cV}$  and the system continues to be in equilibrium  $\therefore$  nothing happens.
- Therefore for using Le-Chatlier's principle, convert the expression of  $K_p$  and  $K_c$  into basic terms and then see the effect of various changes.



on increase in temperature

- a) If  $\Delta H^\circ$  is +ve (endothermic), reaction goes more towards the forward direction and vice – versa
- b) if  $\Delta H^\circ$  is –ve (exothermic), the reaction goes in the reverse direction.
  - i. Increase in temperature will shift the reaction towards left in case of exothermic reactions and right in endothermic reactions.
  - ii. Increase of pressure (decrease in Volume will shift the reaction to the side having fewer moles of the gas; while decreases of pressure (increase in volume) will shift the reaction of the side having more moles of the gas.
  - iii. If no gases are involved in the reaction higher pressure favours the reaction to shift towards higher density solid or liquid.

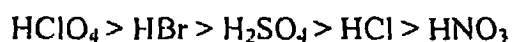
## EQUILIBRIUM – II

Dr. R.K. Parashar

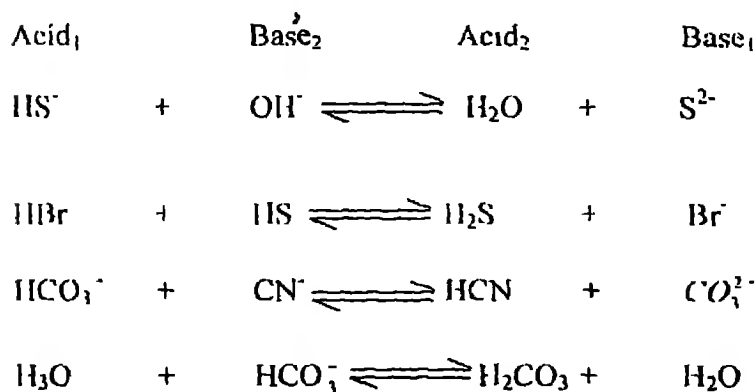
### A. VARIOUS THEORIES REGARDING ACIDS & BASES

- (i) **Arrhenius Theory** . According to Arrhenius, substances producing  $H^+$  ions in solution are acids and those producing  $OH^-$  ions in solution are bases. Therefore, substances like  $H_2O$ ,  $HCl$ ,  $H_2SO_4$ ,  $CH_3COOH$  etc are acids and the ones like  $NH_4OH$ ,  $NaOH$ ,  $KOH$ ,  $H_2O$  etc. are bases.
- (ii) **Bronsted – Lowry Theory** : In 1923, Bronsted and Lowry independently defined acids as proton donors, and bases as proton acceptors. For aqueous solutions the definition does not vary much for acids from the Arrhenius theory but it widens the scope of bases. In this, the bases need not contain  $OH^-$  ions and simply have to accept protons. So ions like  $Cl^-$ ,  $CH_3COO^-$ ,  $Br^-$  etc. which do not contain  $OH^-$  ions can be considered as bases under this definition.

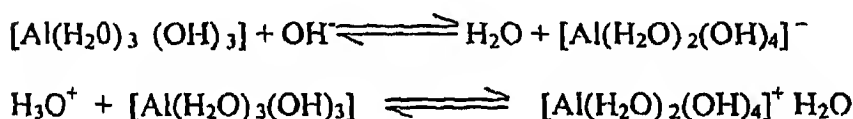
**Leveling Solvents:** Whenever an acid is dissolved in water, it acts as an acid only if the solvent acts as a base. That is, if we dissolve acids like  $HCl$ ,  $HNO_3$  etc in water, their acidic strength is almost the same since water acts as a base for both these acids. In fact, it is known that all strong acids show equal acidic strength when dissolved in water. This is because, water acts as a base to all these acids and thus forces them to donate almost the same amount of protons irrespective of their chemical nature. Since water levels the acidic strength of strong acids, it is referred to as a leveling solvent. In order to measure the strength of strong acids, they are dissolved in glacial acetic acid and the amount of protons measured by conductometry. It is found that the strength of acids varies as



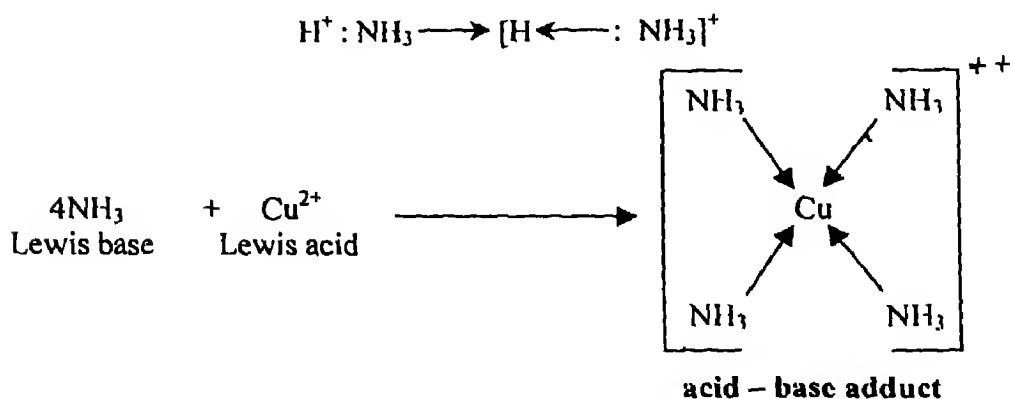
- (iii) **Amphiprotic species:** Many molecules and ions can behave like water and may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic eg.



The hydroxides of metals near the boundary between metals and non-metals in the periodic table, are amphiprotic and so react either as acids or as bases,



- (iv) **Lewis Theory:** Lewis developed a definition of acids and bases that did not depend on the presence of protons, nor involve reactions with the solvent. He defined acids as materials which accept electron pairs, and bases as substances which donate electron pairs. Thus a proton is Lewis acid and ammonia is Lewis base since, the lone pair of electrons on the nitrogen atom can be donated to a proton:



**Conditions to be a Lewis Acid:**

- (i) Compounds whose central atoms have an incomplete octet e.g.  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{GaCl}_3$  etc.
- (ii) Compounds in which the central atom has available d-orbital and may acquire more than an octet of valence electrons.  
 E.g.  $\text{SiF}_4 + 2\text{F}^- \longrightarrow \text{SiF}_6^{2-}$   
 Other examples are  $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{SeF}_6$ ,  $\text{TeCl}_4$
- (iii) All simple cations.  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  etc.

**Conditions to be a Lewis Base:**

- (i) All simple negative ions  $\text{Cl}^-$ ,  $\text{F}^-$  etc.
- (ii) Molecules with unshared pair of electrons,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  etc.
- (iii) Multiple bonded compounds which form co-ordination compounds with transition metals. e.g.  $\text{CO}$ ,  $\text{NO}$ ,  $\text{CH}\equiv\text{CH}$ ,  $\text{CH}_2=\text{CH}_2$

**THE pH SCALE:**

S.P.L. ~~Sorrenson~~ in 1909 introduced a logarithmic scale called pH scale to measure the acidic and basic natures of acids and bases respectively. It is given as  $\text{pH} = -\log [\text{H}^+]$  when  $[\text{H}^+]$  of a solution is higher than its  $[\text{OH}^-]$  the solution is said to be acidic while when the  $[\text{OH}^-]$  is higher than the  $[\text{H}^+]$  the solution is basic pH can also be negative. This is when concentration of  $\text{H}^+$  (rather the activity) is more than one.

**IONIZATION OF WATER**

Pure water is very weakly ionized to give  $\text{H}^+$  and  $\text{OH}^-$  that is,  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ . As can be seen water exists in equilibrium with the  $\text{H}^+$  and  $\text{OH}^-$  ions. Moreover from the law of mass action (which states that for a reversible reaction at equilibrium the ratio of the product of the concentrations of products to the product of the concentrations of the reactants is a constant at a given temp.).

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K$$

K has a value of  $\frac{10^{-14}}{55.5}$  at  $25^{\circ}\text{C}$  the concentration of pure water at  $25^{\circ}\text{C}$  is 55.5 moles/litre (this is because, 1 litre of water which is 1000 C.C. has a weight of 1000gm assuming the density of water to be 1 gm/cc. Therefore, the no. of moles in 1 litres of water is  $1000/18 = 55.5$ )

$$\text{Therefore } [H^+][OH^-] = K [H_2O] = \frac{10^{-14}}{55.5} \times 55.5 = 10^{-14}$$

This value of  $10^{-14}$  is called the ionic product of water and given the symbol  $K_w$ . As water gives equal amount of  $H^+$  and  $OH^-$ , we have

$$\begin{aligned} [H^+][OH^-] &= 10^{-14} \\ \text{or } [H^+][H^+] &= [H^+]^2 = 10^{-14} \\ \text{therefore } [H^+] &= 10^{-7} \end{aligned}$$

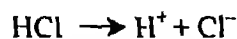
Therefore the pH of water is  $-\log 10^{-7} = 7$  at  $25^{\circ}\text{C}$ . Water is considered to be neutral because it gives equal amounts of  $H^+$  and  $OH^-$ . It is vital to note that in the case of water,  $[H^+]_w [OH^-]_w = 10^{-14}$  where  $[H^+]_w$  and  $[OH^-]_w$  represent the  $H^+$  and  $OH^-$  coming from water. But in case the solution is acidic or basic then the above mentioned equality does not hold good. In such cases it is  $[H^+]_i [H^+]_r = 10^{-14}$  where  $[H^+]_r$  and  $[OH^-]_i$  are the concentrations of  $H^+$  and  $OH^-$  totally present in the solution irrespective of the source

## DETERMINATION OF pH OF ACIDS AND BASES

### (A) Strong Acid:

A strong acid is defined as a substance which completely dissociates to give all the maximum possible  $H^+$  ions that it is capable of giving

For Example



Therefore  $[HCl] = [H^+]$

If we have to find the pH of  $10^{-4}\text{M}$  HCl,

$$[HCl] = [H^+] \quad \therefore \text{pH} = -\log 10^{-4} = 4.$$

Now to find the pH of  $10^{-7}$  M HCl, by applying the above logic, the pH would come out to be 7. This is not possible since the solution of HCl is acidic and it should have pH less than 7. The error that is made here is that, only that  $[H^+]$  which comes from acid is being considered, whereas the  $H^+$  from acid and water should be taken into account. To do this we must not add  $10^{-7}$  M as the contribution of water because water would give less than this amount in the presence of HCl. This is because of common ion effect, which states that when a common ion is added to an equilibrium mixture, the equilibrium shifts in that direction where the common ion gets consumed.

Assuming that  $a$  is the amount of  $H^+$  (or  $OH^-$ ) coming from water. In the case of pure water.

$$a \times a = 10^{-14} \quad \text{----- (1)}$$

In the case of  $10^{-7}$  M HCl, the total  $[H^+]$  will be  $(10^{-7} + a)$  if  $a$  is the amount of  $H^+$  coming from water.

Since  $[OH^-] = a'$ .

$$[H^+]_T [OH^-]_T = (10^{-7} + a') \times a' = 10^{-14} \quad \text{----- (2)}$$

Where  $[H^+]_T$  is the total  $H^+$  coming from both acid and water.

Therefore  $a'$  (the  $[H^+]$  coming from water in the presence of  $10^{-7}$  M HCl) can be calculated from equation (2) and therefore the total  $[H^+]$  would be equal to  $[H^+]_T = a' + 10^{-7}$  and  $pH = -\log [H^+]_T$ .

#### Note

In order to figure out when to take the contribution of water, it should be noted that when  $[H^+]_A \geq 10^{-6}$  M, Water contribution need not be taken and when  $[H^+]_A < 10^{-6}$  M, water contribution should be taken.

### Weak Acids:

By definition weak acids are acids which dissociate weakly or feebly in water. For example  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ . The equilibrium constant is represented as  $K_a$ .

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

If we start with 'C' moles of acetic acid and  $\alpha$  is the degree of dissociation which is defined as the number of moles of acetic acid which dissociates from one mole of acetic acid, then the no. of moles dissociated would be ' $C\alpha$ '



Initial	C	0	0
At eqb,	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Generally, for weak acids ' $\alpha$ ' is very small and to a reasonable approximation we can neglect  $\alpha$  in comparison to 1.

$$K_a = C\alpha^2; \alpha = \sqrt{\frac{K_a}{C}}; \text{ since } [\text{H}^+]_A = C\alpha = C \times \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

Where  $[\text{H}^+]_A$  is the  $[\text{H}^+]$  coming from weak acid. Again if  $[\text{H}^+]_A < 10^{-6}$  M, we must take into account  $\text{H}^+$  coming from water.

Let us follow the above discussion and calculate the pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH}$  with  $K_a = 1.8 \times 10^{-5}$ . Following the above procedure

$$[\text{H}^+]_A = \sqrt{1.8 \times 10^{-5} \times 10^{-6}} = 4.24 \times 10^{-6}$$

$$\begin{aligned} \text{pH} &= -\log 4.24 \times 10^{-6} \\ &= 6 - \log 4.24 = 6 - 0.6274 = 5.37 \end{aligned}$$

If one compares this with the pH of  $10^{-6}$  M HCl, we find that the pH of acetic acid is less than that of HCl (which is 6) with the same concentration. This would mean that acetic acid gives more  $H^+$  ions than HCl for the same concentration in spite of it being a weak acid compared to that of HCl. This is not possible and so evidently there is some error. Let us calculate the degree of dissociation

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{10^{-6}}} = 4.24$$

But we know that  $\alpha$  cannot be more than 1. This means that the error has cropped up when we neglected  $\alpha$  in the denominator of the expression  $\frac{C\alpha^2}{1-\alpha} = K_a$ . This is so because without knowing  $\alpha$  one cannot neglect it in comparison to 1. So,  $\alpha$  has to be calculated by keeping it in the denominator.

$$10^{-6}\alpha^2 + 1.8 \times 10^{-5}\alpha - 1.8 \times 10^{-5} = 0$$

From this  $\alpha$  works out to be,  $\alpha = 0.95$ .

This means  $[H^+]_A = C\alpha = 0.95 \times 10^{-6} = 9.5 \times 10^{-7}$  M

$$pH = -\log 9.5 \times 10^{-7} = 7 - \log 9.5 = 7 - 0.9777 = 6.02.$$

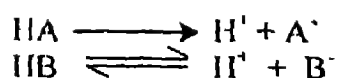
**Note.** In order to figure out when to neglect  $\alpha$  in the denominator, first always calculate  $\alpha$  by the expression

$$\alpha = \sqrt{\frac{K_a}{C}}$$

If  $\alpha$  from this is  $> 0.1$  then  $\alpha$  cannot be neglected and has to be calculated by the quadratic equation. If  $\alpha \leq 0.1$ ,  $\alpha$  can be ignored in comparison to 1.

### (C) Strong Acid + Weak Acid

Let us assume that we have a strong acid HA and a weak acid HB. Let the concentration of HA and HB be  $C_1$  and  $C_2$  respectively and let the dissociation constant of HB be  $K_a$



[ $\alpha$  is the degree of dissociation of HB in the presence of HA]

$$C_2(1-\alpha) \quad C_2\alpha + C_1 \quad C_2\alpha$$

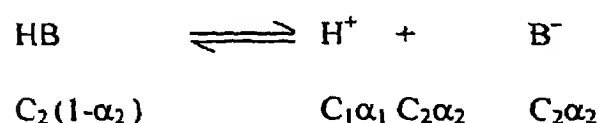
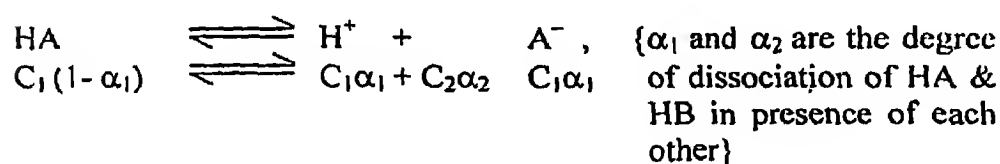
$$[\text{HB}] = C_2(1-\alpha); [\text{B}] = C_2\alpha; [\text{H}^+] = C_2\alpha + C_1 \text{ (total } \text{H}^+ \text{ concentration)}$$

$$\text{Therefore } K_a = \frac{[\text{H}^+][\text{B}]}{[\text{HB}]} = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)}$$

Solving this equation we can get the value of  $\alpha$  and then determine the  $[\text{H}^+]$  and find the pH.

#### (D) TWO WEAK ACIDS

If we have two weak acids, HA and HB with concentration  $C_1$  &  $C_2$  and dissociation constants  $K_{a1}$  and  $K_{a2}$ , then



$$[\text{HA}] = C_1(1-\alpha_1); \quad [\text{A}] = C_1\alpha_1; [\text{HB}] = C_2(1-\alpha_2)$$

$$[\text{B}^-] = C_2\alpha_2 \text{ AND } [\text{H}^+] = C_1\alpha_1 + C_2\alpha_2$$

$$K_{a1} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(C_1\alpha_1 + C_2\alpha_2)C_1\alpha_1}{C_1(1-\alpha_1)}$$

$$K_{a2} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} = \frac{(C_1\alpha_1 + C_2\alpha_2)C_2\alpha_2}{C_2(1-\alpha_2)}$$

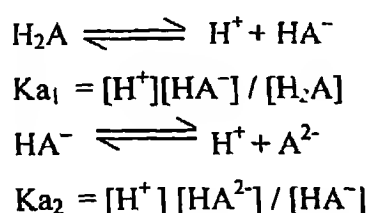
The above two equations can be solved for  $\alpha_1$  and  $\alpha_2$  from which the  $\text{H}^+$  concentration can be calculated and the pH can be found out

NOTE: The pH of bases will be calculated just like we do for acids, with the difference that instead of  $H^+$  ions we would have  $OH^-$  ions, instead of  $K_a$ , we would have  $K_b$  and instead of pH, we would first calculate pOH. Then pH can be calculated as  $pH = 14 - pOH$ .

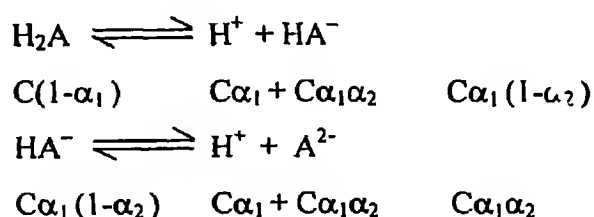
### (E) Dibasic and Polyprotic Weak Acids

Dibasic acid is an acid which has the capacity to give two  $H^+$  ions per molecule of the acid eg  $H_2SO_4$ ,  $H_2S$  etc

Let us take for example a dibasic weak acid  $H_2A$ . It dissociates as (assuming both dissociations are weak)



If the initial concentration of  $H_2A$  is  $C$  and  $\alpha_1$  and  $\alpha_2$  are the degrees of dissociation for the first and second dissociations.



Before proceeding it is important to understand that all equilibria exist with respect to the total no. of ions in the solution that is  $[H_2A] = C(1-\alpha_1)$ ,  $[HA^-] = C\alpha_1$  initially. As the second dissociation comes to equilibrium  $[HA^-]$  becomes  $C\alpha_1\alpha_2$  and  $[A^{2-}] = C\alpha_1\alpha_2$ . From the first dissociation  $[H^+]$  is  $C\alpha_1$  and from the second dissociation  $[H^+] = C\alpha_1\alpha_2$  so the  $H^+$  total concentration from the acid becomes  $C\alpha_1 + C\alpha_1\alpha_2$ .

$$K_{a1} = [H^+][HA^-] / [H_2A] = (C\alpha_1\alpha_2 + C\alpha_1)(C\alpha_1(1-\alpha_2)) / C(1-\alpha_1)$$

$$K_{a2} = [H^+][A^{2-}] / [HA^-] = (C\alpha_1\alpha_2 + C\alpha_1)(C\alpha_1\alpha_2) / C\alpha_1(1-\alpha_2)$$

From the above two equations we can solve for  $\alpha_1$  and  $\alpha_2$  and calculate the  $[H^+]$  and find the pH. A similar treatment can be given to polyprotic acids.

## DETERMINATION OF pH DUE TO HYDROLYSIS

When a salt is dissolved in a solvent it first dissociates into its constituent ions. This process is called dissolution. Now, if these ions chemically react with water, the process is called hydrolysis. The salts that undergo hydrolysis after dissolution are:

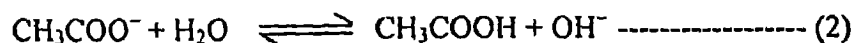
1. Salts of weak acids + strong bases
2. Salts of weak bases + strong acids
3. Salts of weak acids + weak bases

### (A) Salts of Weak Acid + Strong Base

Let us consider the weak acid to be acetic acid and the strong base to be NaOH

Therefore,  $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ . The salt would dissolve as,  $CH_3COONa \rightarrow CH_3COO^- + Na^+$  ----- (1)

If 'C' is the concentration of the salt, then 'C' would be the concentration of  $CH_3COO^-$ . Now, the acetate ion is hydrolysed by water to give acetic acid and  $OH^-$



$Na^+$  does not get hydrolysed because it would react with water to produce NaOH which is a strong base and would completely decompose to give  $Na^+$  and  $OH^-$ . If  $\alpha$  is the degree of hydrolysis, we would have  $[CH_3COO^-] = C(1 - \alpha)$

$[\text{CH}_3\text{COOH}] = C \alpha$  and  $[\text{OH}^-] = C \alpha$ . The hydrolysis equilibrium is represented by the hydrolysis constant.

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]^2} \text{----- (3)}$$

$$\text{Now } K_w = [\text{H}^+][\text{OH}^-] \text{ and } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\text{Therefore } \frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \text{ Comparing this with (3)}$$

$$\text{We have, } K_h = \frac{K_w}{K_a}$$

$$\text{Therefore } \frac{K_w}{K_a} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Assuming that  $\alpha \ll 1$ , we neglect  $\alpha$  in the denominator.

$$C\alpha^2 = \frac{K_w}{K_a}; \alpha = \sqrt{\frac{K_w}{K_a C}}$$

Since  $[\text{OH}^-] = C\alpha$ , We have,

$$[\text{OH}^-] = C \times \sqrt{\frac{K_w C}{K_a}}$$

$$\text{We are aware that, } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w K_a}{C}}$$

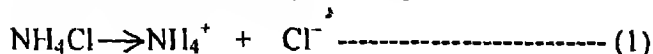
As one can see, the hydrolysis of  $\text{CH}_3\text{COO}^-$  produces  $\text{OH}^-$  ions in the solution.

Note

Whenever the salt of weak acid and strong base is dissolved in water, the solution is basic.

**(B) Salt of Weak Base + Strong Acid**

Let us consider the weak base to be  $\text{NH}_4\text{OH}$  and the strong acid to be  $\text{HCl}$ .



If the concentration of  $\text{NH}_4\text{Cl}$  is 'C'  $[\text{NH}_4^+]$  gets hydrolysed to give  $\text{H}^+$  and  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+ \text{----- (2)}$

If  $\alpha$  is the degree of hydrolysis,  $[\text{NH}_4^+] = C(1-\alpha)$ ;  $[\text{NH}_4\text{OH}] = C\alpha$  and  $[\text{H}^+] = C\alpha$ . The equilibrium constant is represented as  $K_h$

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \text{----- (3)}$$

We know that,  $K_w = [\text{H}^+][\text{OH}^-]$

$$\text{and } K_p = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$\text{Therefore } \frac{K_w}{K_h} = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = K_h \text{ [Comparing with equation (3)]}$$

$$\frac{K_w}{K_h} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

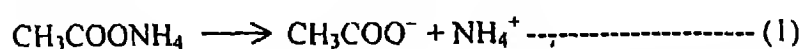
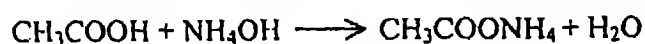
$$\text{Assuming '}\alpha\text{' to be very small compared to 1, } C\alpha^2 = \frac{K_w}{K_h}$$

$$\alpha = \sqrt{\frac{K_w}{K_h C}} \text{ Since } [\text{H}^+] = C\alpha = C \sqrt{\frac{K_w}{K_h C}} = \sqrt{\frac{K_w}{K_h C}}$$

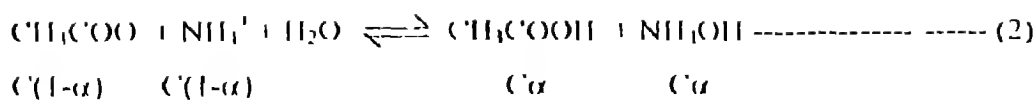
Note. Whenever the salt of a weak base and strong acid is dissolved in water, the solution is acidic.

**(C) Salt of A Weak Acid & Weak Base**

Let the weak acid be  $\text{CH}_3\text{COOH}$  and the weak base  $\text{NH}_4\text{OH}$ .



if the concentration of salt is 'C' then  $[\text{CH}_3\text{COO}^-] = C$ ,  $[\text{NH}_4^+] = C$



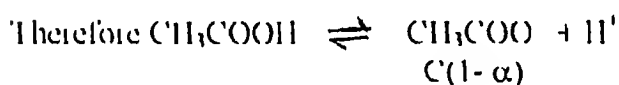
$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad (3)$$

It can be proved that  $K_b = \frac{K_w}{K_a K_b}$

$$\text{Therefore } \frac{C\alpha \times C\alpha}{C(1-\alpha) \times C(1-\alpha)} = \frac{K_w}{K_a K_b}$$

$$\frac{\alpha}{1-\alpha} = \sqrt{\frac{K_w}{K_a K_b}}$$

The acetic acid formed would partially decompose to give  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$ . But because of common ion effect (that is due to the unhydrolysed  $\text{CH}_3\text{COO}^-$ ) it is possible to neglect the acetate ion coming from  $\text{CH}_3\text{COOH}$ .



$$K_a = \frac{C(1-\alpha)[\text{H}^+]}{C\alpha}$$

$$K_a = \frac{[\text{H}^+]}{\alpha} \quad (\text{Neglecting } \alpha)$$

$$[\text{H}^+] = K_a \alpha = K_a \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_a K_w}{K_b}}$$

NOTE: if  $K_a > K_b$ , the solution would be acidic, if  $K_a < K_b$ , the solution would be basic and if  $K_a = K_b$ , the solution would be neutral.

## BUFFER SOLUTIONS

There are three ways in which the pH of a solution can be changed. One way is to add an acid and another way is to add a base and yet another way is to add water. By adding an acid the  $[\text{H}^+]$  increases, so pH changes, by adding a

base,  $[OH^-]$  increases so pH changes and finally by adding water the  $[H^+]$  changes due to increases in the volume of solution.

A buffer solution is one which resists a change in pH due to the addition of an acid or a base. This does not mean that the pH does not change. All it implies is that the pH change would be less than expected. That is, let say we add 10 moles of  $H^+$  to a solution the pH change would correspond to probably say two moles and not 10 moles.

There are three kinds of ~~buffer~~ solutions:

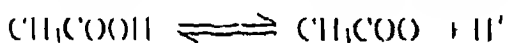
(A) Acid Buffer :

An acid buffer is formed when a weak acid and any salt of the weak acid with a strong base co-exist in a solution.

For example,

$CH_3COOH$  and  $CH_3COONa$ . Let us now understand as to why this system acts as a buffer.

In the solution acetic acid would dissociate to give acetate and  $H^+$ ,



Moreover the salt would completely dissociate to give  $CH_3COO^-$



Because of the acetate coming from the salt, it creates a common ion effect due to which the dissociation of acetic acid decreases. So, we can assume that, acetic acid virtually gives no  $CH_3COO^-$  and that the entire acid remains as  $CH_3COOH$ . Now in the solution we have two important constituents,  $CH_3COO^-$  and  $CH_3COOH$ .

If a strong acid is added to this system, the  $H^+$  ions react with acetate ions to form acetic acid



In fact this reaction proceeds practically to completion. This is because the extent of the reverse reaction i.e.  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$  is given by its  $K_a$  value which is  $\approx 10^{-5}$  therefore the  $K$  for reaction (1) would be  $10^5$ . This indicates that reaction (1) proceeds practically to completion.

Now, let us assume that we have 20 moles of  $\text{CH}_3\text{COO}^-$  in the buffer, and 10 moles of  $\text{H}^+$  is added from outside. 10 moles of  $\text{CH}_3\text{COO}^-$  will be consumed to produce 10 moles of  $\text{CH}_3\text{COOH}$ . Being a weak acid, 10 moles of  $\text{CH}_3\text{COOH}$  cannot give 10 moles of  $\text{H}^+$ . Since 10 moles of  $\text{CH}_3\text{COO}^-$  is left in the solution, it would create a common ion effect and would further suppress the dissociation of  $\text{CH}_3\text{COOH}$ . Because of acetic acid would give only say 2 moles of  $\text{H}^+$ . Therefore the buffer system has resisted the pH change and the pH change corresponds to only 2 moles of  $\text{H}^+$  and not 10 moles which was added.

When a base is added the  $\text{OH}^-$  would react with  $\text{CH}_3\text{COOH}$  to produce  $\text{CH}_3\text{COO}^-$  and  $\text{H}_2\text{O}$ .  $\text{CH}_3\text{COOH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ . The  $K$  for the reverse reaction is given by  $K_b$  which is equal to  $\frac{K_w}{K_a} \left( \approx \frac{10^{-14}}{10^{-5}} = 10^{-9} \right)$  therefore the  $K$  for the forward reaction would be  $10^9$ . This means the forward reaction proceeds practically to completion. How the system resists the pH changes can be looked at from the explanation given earlier for the addition of  $\text{H}^+$ .  
Now, since  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\text{We have } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

In a buffer  $[\text{CH}_3\text{COO}^-] = [\text{Salt}]$ ;  $[\text{CH}_3\text{COOH}] = [\text{Acid}]$

$$\therefore K_a = \frac{[\text{Salt}][\text{H}^+]}{[\text{Acid}]} \quad \text{or} \quad [\text{H}^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

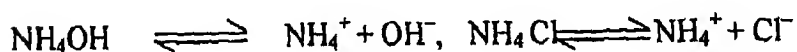
Taking log on both sides and multiplying by -- 1,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

NOTE : One can also see why the addition of water causes no change in pH of a buffer. This is because the volume change caused due to the addition of water effects both [Salt] and [Acid] and the volumes actually cancel

**(B) Basic Buffer:**

A basic buffer results when a weak base and its salt (with strong acid) co-exist in a solution, For example,  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$

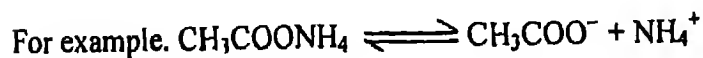


The buffer action can be explained as in the previous case.

$$\text{For a basic buffer, } \text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

**(C) Salt Buffer:**

A salt buffer is a solution of a salt which itself can act as a buffer. Such a salt is the salt of a weak acid and weak base.



When an acid is added, it reacts with  $\text{CH}_3\text{COO}^-$  to produce  $\text{CH}_3\text{COOH}$  and when a base is added, it reacts with  $\text{NH}_4^+$  to produce  $\text{NH}_4\text{OH}$ .

## **SOLUBILITY AND SOLUBILITY PRODUCT**

Solubility of a salt that can be dissolved in 1L of a solution that would make the solution saturated at a given temperature. It can also be explained as the concentration of saturated solution of a salt at a given temperature.

Let us consider a salt AgCl that is dissolved in water. Initially the salt would completely ionize to give  $\text{Ag}^+$  and  $\text{Cl}^-$  ions.  $\text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^-$ . As more and more of AgCl is dissolved, the solution ultimately gets saturated. If now some more AgCl is added to the solution, this undissolved AgCl would be in equilibrium with the ions in the solution.



Since this equilibrium exists,  $K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$

As  $K[\text{AgCl}] = K_c = [\text{Ag}^+][\text{Cl}^-]$

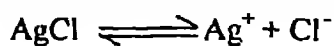
This  $K_c$  is given a special name,  $K_{sp}$ , the solubility product. This means that any solution containing  $\text{Ag}^+$  &  $\text{Cl}^-$  ions, irrespective of how it is formed, cannot have their ionic product more than the  $K_{sp}$  of AgCl.

$\therefore$  If the product of the ions (ionic product) is less than the  $K_{sp}$ , more of the salt dissolves. If the ionic product is equal to  $K_{sp}$ , the solution is saturated. And if it is greater than  $K_{sp}$ , the salt would precipitate out.

## IMPORTANT CASES OF CALCULATING SOLUBILITY OF A SALT

In this section we deal with some of the most important cases of calculating the solubility of a salt.

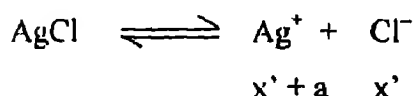
(a) Solubility of a salt of strong acid and a strong base (AgCl) in pure water



Let the solubility of the salt be  $x$  moles per litre, then at equilibrium. the concentration of  $\text{Ag}^+$  equals  $x$  moles per litre and that of  $\text{Cl}^-$  is also  $x$  moles per litre

$$\therefore x^2 = K_{sp} \quad x = \sqrt{K_{sp}}$$

- (b) Solubility of a salt of strong acid and a strong base ( $\text{AgCl}$ ) in a solution which already contains a common ion.  $[(\text{Ag}^+) = a \text{ moles/L}]$



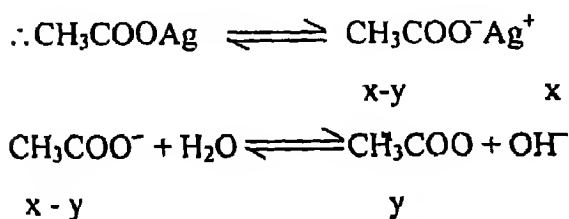
Let the solubility of  $\text{AgCl}$  in the presence of common ion be  $x'$ . Therefore concentration of  $\text{Ag}^+ = x' + a$  and  $\text{Cl}^-$  concentration is  $x'$ . Therefore  $(x' + a) \times x' = K_{sp}$

The  $x'$  calculated here will be less than the value of  $x$  calculated earlier.

- (c) Solubility of a salt of weak acid and strong base ( $\text{CH}_3\text{COOAg}$ ) in pure water



Since it is a salt of weak acid and strong base, it will also get hydrolysed.



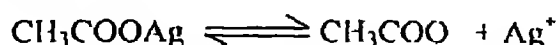
Let The solubility of the salt be  $x$  mole/L and the amount of  $\text{CH}_3\text{COO}^-$  getting hydrolysed by  $Y$  moles/L

$$\begin{aligned} [\text{CH}_3\text{COO}^-] &= (x-y) \text{ moles/L} \\ [\text{Ag}^+] &= x \text{ moles/L} \\ [\text{CH}_3\text{COOH}] &= y \text{ moles/L} \\ [\text{OH}^-] &= y \text{ moles/L} \\ (x-y) \times x &= K_{sp} \end{aligned}$$

$$\frac{y^2}{(x-y)} = K_h = \frac{K_w}{K_a}$$

Solving these two equations we can find the value of x.

- (d) Solubility of a salt of weak acid and strong base ( $\text{CH}_3\text{COOAg}$ ) in an acidic buffer solution.



Since the solution is acidic,  $\text{CH}_3\text{COO}^-$  would take up the free available  $\text{H}^+$  ions and produce acetic acid.



Let the solubility of the salt be  $x'$  moles/L and let the concentration of  $\text{CH}_3\text{COO}^-$  combined with  $\text{H}^+$  be  $y'$

$$\therefore [\text{CH}_3\text{COO}^-] = x' - y', [\text{CH}_3\text{COOH}] = y', [\text{Ag}^+] = x'$$

$$\therefore x' (x' - y') = K_{sp}$$

$$\frac{y'}{(x' - y')[\text{H}^+]} = K_a^{-1}$$

Solving these two equations, the value of  $x'$  may be calculated it can be seen that this value of  $x'$  would be more than that of  $x$  (solubility in pure water)

- (e) Solubility of a salt of a weak acid and strong base ( $\text{CH}_3\text{COOAg}$ ) in a basic buffer



Here both the hydrolysis and combination of  $\text{CH}_3\text{COO}^-$  with  $\text{H}^+$  can be ignored. This is because, since the solution is basic the  $[\text{H}^+]$  will be less and very less amount of  $\text{CH}_3\text{COO}^-$  would react with  $\text{H}^+$  and moreover the hydrolysis would get suppressed by all the already existing  $\text{OH}^-$  ions.

Let the solubility of  $x''$ .

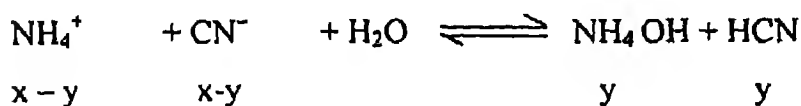
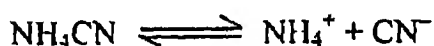
$$\therefore x^{-2} = K_{sp}$$

Note The solubility of a salt of weak acid and strong base will be highest in an acidic solution, then in pure water and then in a base solution

(f) Solubility of salt of strong acid and weak base ( $C_6H_5NH_3^+ Cl^-$ )

The solubility of such a salt may be calculated in the same manner in different conditions as was done in the case of  $CH_3COOAg$ . It would be found that  $C_6H_5NH_3^+ Cl^-$  has the highest solubility in a basic solution, then in pure water and then in an acidic solution

(g) Solubility of a salt of weak acid and weak base ( $NH_4CN$ ) in pure water



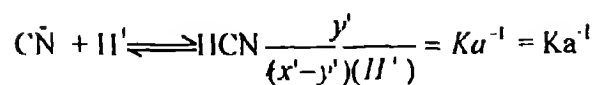
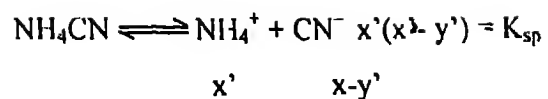
$$\therefore (x-y)^2 = K_{sp}$$

$$\frac{y^2}{(x-y)^2} = \frac{K_w}{K_a K_b}$$

Solving these two equations, one can find the solubility of the salt.

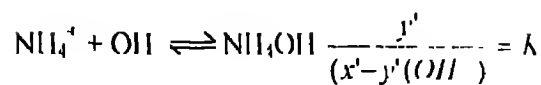
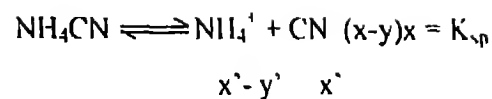
(h) Solubility of a salt of weak acid and weak base in an acidic buffer and in a basic buffer.

### Acidic Buffer



$$x' - y' \quad y'$$

### Basic Buffer



$$x' - y' \quad y'$$

### Common Ion effect :

The suppression of the dissociation of a weak acid or a weak base on the addition of its own ion is called common ion effect.



# Electro Chemistry

## Introduction

The branch of science, which deals with the relationship between electrical energy and chemical energy and inter conversion of one form into another is called Electro Chemistry

## Overview

This module will give account of following topics

- 1) Types of Electro Chemical Changes
- 2) Independent Migration of ions
- 3) Voltic Cell/Nernst Equation
- 4) EMF Series.
- 5) Electro lysis
- 6) Corrosion
- 7) Commercial Cell
- 8) Activity No 1 – Construction of Standard Orange Electrode
- 9) Activity No 2 – Construction of Dry Cell

## Types of Electro Chemical Changes

### Electrolysis

Changes in which electrical energy causes chemical reactions

Electro Chemical changes in which electrical energy is produced from chemical change.

Device: Electrolytic Cell

Device: Electro Chemical Cell  
Galvanic Cell  
Voltaic Cell

**Electrolytes:** The substances, which furnish ions in solution and conduct electricity, are called Electrolytes.

### Types of electrolytes:

Electrolytes can be classed in following ways

#### (I) True Electrolytes

In these cations and anions do exist in their pure normal states and also conduct electricity in the molten state

Ex NaCl, KCl

#### Potential Electrolytes

Do not conduct electricity in their pure state but conduct electricity when dissolved in water

Ex HCl, CH<sub>3</sub>COOH, CO<sub>2</sub>, NH<sub>3</sub>

**(II) Strong Electrolytes and Weak Electrolytes:**

The term strong and weak are relative. A strong electrolyte may be weak as compared to another one similarly a weak electrolyte may be stronger as compared to some other one.

The behaviour of an electrolyte also depends on the nature of the solvent.

**For Example:**

NaCl behaves as strong electrolyte while  $\text{CH}_3\text{COOH}$  is weak electrolyte in water.

On the other hand, when dissolved in ammonia both the NaCl and  $\text{CH}_3\text{COOH}$  show comparable behaviour towards electricity.

The behaviour of Electrolytes is therefore, compared by studying their conductivities in a common solvent.

**Kohlrausch's Law  
(Of Independent Migration of Ions)**

At infinite dilution when the dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.

$$\lambda_m^\alpha = \nu_+ \lambda_+^\alpha + \nu_- \lambda_-^\alpha$$

Where  $\nu_+$  = No. of cations/formula Unit of electrolyte

$\nu_-$  = No. of anions/formula unit of electrolyte

**Applications of Kohlrausch's Law**

- (1) Calculation of molar conductance at infinite dilution for weak electrolyte
- (2) Calculation of degree of dissociation of weak electrolyte

$$\alpha = \frac{\lambda_m^c}{\lambda_m^\alpha}$$

$\lambda_m^c$  = Molar conductance of solution at any concentration

$\lambda_m^\alpha$  = Molar conductance at infinite dilution

- (3) Calculation of dissociation constant (K) of weak electrolyte

$$K = \frac{C \alpha^2}{(1 - \alpha)} \quad \begin{array}{l} \text{where } C = \text{Concentration} \\ \alpha = \text{Degree of dissociation} \end{array}$$

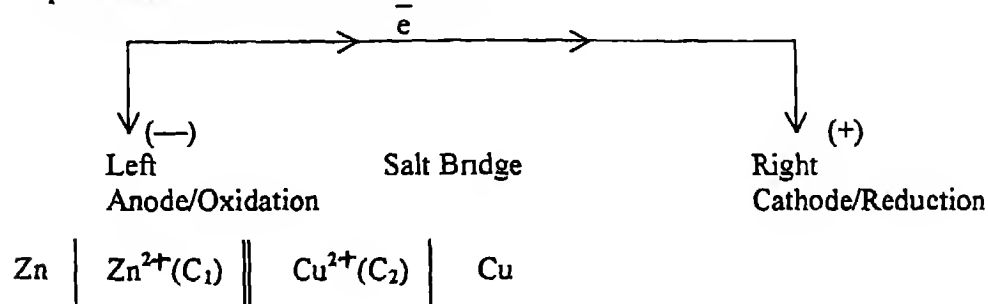
### Voltaic Cell

The devices in which electrical energy is produced from chemical reactions are called electro chemical cells/galvanic cells/voltaic cells

In these cells, oxidation and reduction reactions occur in separate containers called half cells, and the reaction is spontaneous

**Example:** Cu - AgNO<sub>3</sub> cell  
Zn - CuSO<sub>4</sub> cell  
Ni - AgNO<sub>3</sub> cells

**Representation of electrochemical cells:**



Where  $C_1$  and  $C_2$  = Concentration of solution

**Role of salt bridge:**

- (i) It maintains internal connection between the solutions of the two half-cells of a galvanic cell but it prevents a direct contact
- (ii) It maintains electro neutrality in the solutions of the half-cells
- (iii) It minimizes the liquid junction potential as the two solutions are prevented from mixing into one another

**Electrode Potential:**

"The ability of an electrode to attract the electrons or the capacity of an electrode to resist the removal of the electrons is measured in terms of Electrode Potential or half cell potential"

"The work done to bring a unit -ve charge from infinite distance to the point of interest is called Electrical Potential. It is also equal to the work done to take a unit charge from the same point of interest to infinity"

$$\begin{aligned}
 E &= W(\text{Elect})/Q & (E = \text{Electrical potential}) \\
 E &= W/nF & Q = \text{Charge} \\
 W &= nFE & W = \text{work} \\
 W &= nFE \\
 \Delta G &= W(\text{net}) \\
 \Delta G &= -nFE
 \end{aligned}$$

**Standard Electrode Potential:**

"The difference of the electrode potential of the half cell under consideration and the electrode potential of a reference standard hydrogen electrode is called standard electrode potential of the half cell in question "

**EMF (Electro Motive Force/Cell Potential (Potential Difference)**

'The difference between electrode potentials of the two electrodes constituting an electro chemical cell is known as cell potential The emf of a cell may be defined as the potential difference between two electrodes of the cell when either no or negligible current is allowed to flow in the circuit'

**Standard Hydrogen Electrode (reference electrode)**

Reversible Hydrogen electrode has been accepted as a reference electrode.

**Reference Electrode:** The electrode, which is used to conduct a galvanic cell for the evaluation of the electrode potential of another half-cell is called reference electrode By convention SHE is assigned a zero electrode potential  $E^0 = 0$

It is not always convenient to use SHE as reference electrode because of experimental difficulties in its preparation and use Some of them are.

- (I) It is difficult to maintain unit concentration of  $H^+$  ions
- (II) The hydrogen electrode gets poisoned even in the presence of traces of impurities.
- (III) It is difficult to maintain 1 atm pressure of  $H_2$  gas uniformly for a long time

Therefore, some other secondary reference electrodes are

- (a) Saturated calomel  $Hg/Hg_2Cl_2(s)/KCl$  (saturated)  
 $E^0 = 0.2415V$  at  $25^\circ C$
- (b) 1N calomel  $Hg/Hg_2Cl_2(s)/KCl(1N)$   
 $E^0 = 0.2800V$

**Electro Chemical Series**

"The arrangement of elements in order of increasing reduction potential values is called electro chemical series "

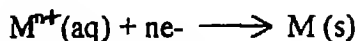
**Application of EMF Series:**

- (1) Relative strengths of oxidizing and reducing agent
- (2) Calculation of the EMF of the cell
- (3) Predicting feasibility of the reaction
- (4) To predict whether a metal can liberate hydrogen from acid or not

## NERNST EQUATION

The relation representing the variation of electrode potential (and cell potential) with the concentration of ions is called Nernst equation.

For a half cell reaction



The Nernst equation is written as

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$= E^0 - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

Since M is a solid sps,  $[M] = 1$  by convention

and equation can be written as

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

Where E = Electrode potential

$E^0$  = Standard Electrode Potential

R = Gas Constant =  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

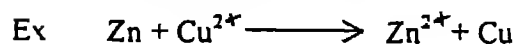
T = temp. in Kelvin

F =  $96500 \text{ C mol}^{-1}$

n = Moles of electrons involved in the reaction.

**Nernst equation for a galvanic cell:**

$$E_{(Cell)} = E_R - E_L = E_{Cathode} - E_{anode}$$



$$E_R = E^0_{(Cu^{2+}/Cu)} - \frac{RT}{nF} \ln \frac{1}{[Cu^{2+}]}$$

$$E_L = E^0_{(Zn^{2+}/Zn)} - \frac{RT}{nF} \ln \frac{1}{[Zn^{2+}]}$$

$$E_{cell} = [E^0_{(Cu^{2+}/Cu)} - E^0_{(Zn^{2+}/Zn)}] - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

## Electrolysis

The phenomenon of chemical change taking place by the passage of electrical energy from an internal source is called electrolysis.

### Laws of Electrolysis

#### 1. First Law

The amount of any substance liberated at the electrode is directly proportional to the quantity of electricity passed through the electrolyte solution

#### 2. Second Law

When the same quantity of electricity is passed through different electrolyte solutions connected in the series, the weights of different substances produced at the electrodes are proportional to their equivalent weights

The charge on one mole of  $e^-$  is called 1 Faraday

$$\text{Charge on one mole of electrons} = 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \text{ C}$$

$$= 96485 \text{ C/mol}$$

$$\approx 96500 \text{ C/mol}$$

$$\text{Charge on } n \text{ mole of } e^- = nF$$

## Corrosion

When metal reacts with air & water to form undesirable compounds (usually oxides) The process is called corrosion

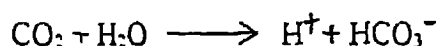
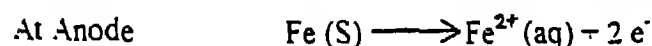
OR

The corrosion is a process of deterioration of metal as a result of its reaction with air & water surrounding it. In case of iron, corrosion is called Rusting

### Mechanism of Rusting of Iron (Electrochemical Theory):

The non-uniform surface of metal or impurities present in iron behaves like small electric cells (called corrosion couples) in the presence of water containing dissolved  $O_2$  &  $CO_2$  (behaving as electrolytic solution)

Pure iron acts as anode & impure portions are cathodes

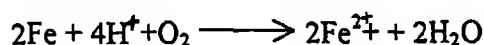
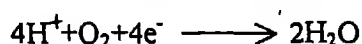


At Cathode.  $\text{H}^+ + \text{e}^- \longrightarrow \text{H}$

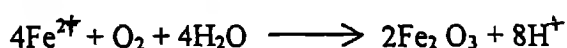


Overall cathode reaction  $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$

Overall cell reaction  $\text{Fe (s)} \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \times 2$



$\text{Fe}^{2+}$  ions oxidized further by atmospheric oxygen



## Commercial Cells

Battery is an arrangement of electro chemical cells used as an energy source

### Characteristics of Battery

- (1) It should be light and compact so that it can be easily transported
- (2) It should have reasonably long life both when it is being used and when it is not used
- (3) The voltage of the battery should not vary appreciably during its use

### Types of commercial cells:

	Primary Not chargeable	Secondary Can be recharged
Ex:	1 Dry Cell	1. Lead Storage Battery
	2 Mercury Cell	2 Ni-Cd Storage Cell

### Primary Cells:

#### [a] Dry Cell:

- (1) The term dry cell is something of a misnomer. The cell is not dry in the sense of being free of water, but rather it contains no fluids. The water it does contain is absorbed into a felt pad that keeps it from flowing.
- (2) The dry cell is often called a Zn-Carbon battery after the materials of its electrodes. This name too is misleading, because while the Zn electrode is active, being consumed during discharge of the battery, the carbon electrode is inert.
- (3) The dry cell also called Leclanche cell, after George Leclanche, the French Engineer who demonstrated a forerunner around 1867.

The original Leclanche cell consisted of a Zn electrode dipping into an  $\text{NH}_4\text{Cl}$  solution and a carbon electrode dipping into  $\text{MnO}_2$ .

Gassner, who substituted a moist paste of  $\text{NH}_4\text{Cl}$  for the solution, and formed the Zn electrode into a container for the cell, introduced the "Dry Cell" in 1888.

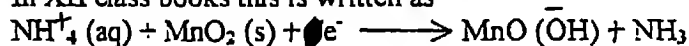
**Mechanism: Anode Reaction**  $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$

At the cathodes (Carbon electrode)  $\text{MnO}_2$  is reduced. The actual process involved at the carbon electrode has been a subject of debate.

Kozawa ~~and Powers~~ postulated a single solid, phase, Proton-electron mechanism, in which the  $\text{MnO}_2$  crystal lattice accepts the Protons and electrons. Upon continued discharge the  $\text{Mn}^{3+}$  and  $\text{OH}^-$  concentrations increase, suggesting the following cathodes reaction.

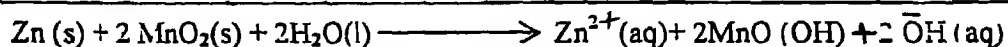


In XII class books this is written as



This is the prevalent reaction at a slow discharge rate but other discharge reactions have been found and are dependent upon Electrolyte concentration, discharge temperature and type of  $\text{MnO}_2$  used.

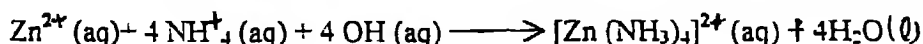
**Overall Cell Reaction:**



The hydroxide ions produced at the carbon electrode migrate toward the zinc electrode, carrying negative charge from the carbon electrode back to the Zn electrode.

The zinc ions produced at the zinc electrode migrate in the opposite direction.

Where  $\text{OH}^-$  and  $\text{Zn}^{2+}$  ions meet, a complex of zinc and  $\text{NH}_3$  forms from the  $\text{NH}_4\text{Cl}$ .



**Important points in construction of dry cell:**

1. The inner surface of the zinc can is coated with a paste of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$ , starch. Starch is used to keep the paste stiff.
2. The zinc can is fitted with a mixture of  $\text{MnO}_2$  and powdered graphite.

The powdered graphite is used to increase the electric conductivity of the mixture.

The ratio of  $\text{MnO}_2$  to graphite powder typically varies from 3:1 to 10:1.

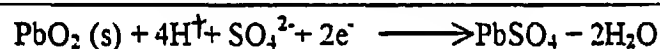
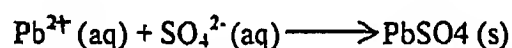
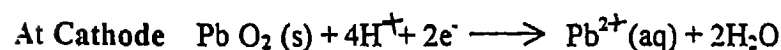
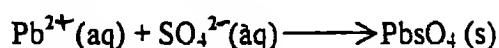
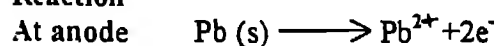
In cells for high current demand, a reaction of 1:1 is common.

- General-purpose batteries use  $\text{MnO}_2$  obtained from natural  $\text{MnO}_2$ , whereas heavy-duty batteries use  $\text{MnO}_2$  produced by the electrolysis of hot  $\text{MnSO}_4$  solution, which is more uniform
- Ammonia, which is produced by reaction of  $\text{NH}_4\text{Cl}$  with  $\text{OH}^-$ , reacts with  $\text{Zn}^{2+}$  ions and  $\text{Cl}^-$  ions, forming tetra ammine zinc (II) ion  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and diammine dichloro zinc (II)  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$ . The accumulation of  $\text{NH}_3$  inside the cell would cause the cell contents to expand & perhaps cause the cell to leak. To minimize the risk of leakage the Zn can is usually clad with steel jacket.

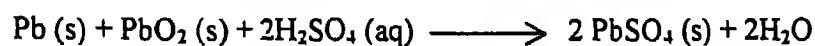
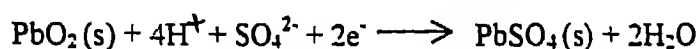
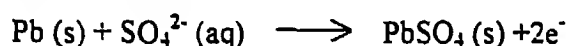
### The Lead Storage Battery:

It was first developed by Raymond Gaston Plante in 1860

#### Reaction



#### Complete cell reaction:



During recharging of the cells bubbles of the gas form at the electrodes. This occurs because the voltage applied to the cell is greater than that needed to charge the cell, namely 2 volts. The over voltage causes the electrolysis of water in the cell, and  $\text{H}_2$  is produced at the cathode and  $\text{O}_2$  gas at the anode. The generation of explosive hydrogen gas mandates that lead storage batteries be charged in well-ventilated areas away from sparks and flames.

### Fuel Cell

The main difference between a conventional electrochemical cell and a fuel cell is that, in a fuel cell, the materials undergoing oxidation at the anode or reduction at the cathode are stored outside the cell. These are not the part of the cell.

**Ex:** Hydrogen/Oxygen fuel cell

Electrolyte ——— acid or base

Hydrogen and oxygen are bubbled through a porous carbon electrode containing suitable catalysis

**Electrode reactions:**

{1} When acid is used as Electrolyte

Cathode. Reduction  $O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$   $E_R^0 = 1.229V$

Anode. Oxidation  $2H_2 - 4e^- \longrightarrow 4H^+$   $E_L^0 = 0.0000$

Overall:  $2H_2 + O_2 \longrightarrow 2H_2O$

$$E_{Cell}^0 = E_R^0 - E_L^0 = 1.229 - 0.0000 = 1.229 V$$

{2} When Alkali (Conc NaOH) as an Electrolyte

Cathode Reduction  $O_2 + 4e^- + 2H_2O(l) \longrightarrow 4OH^-(aq)$

Anode Oxidation  $2H_2 + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

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Overall.  $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Advantages of Fuel Cells over ordinary batteries are

- (a) High efficiency
- (b) Continuous source of energy
- (c) Pollution free working

Now we perform two activities related to Electro Chemical cells to understand the concept practically

## **Activity No. 1**

### **The "Standard" Orange Electrode**

Two holes are cut in an orange, a graphite rod is inserted in one hole, and a gel-filled tube is inserted in the other. The other end of the gel-filled tube is inserted, in turn, in each of several beakers containing solutions and strips of metal. A voltmeter is connected between the metal strip in the beaker and the graphite rod in the orange, and is recorded for each beaker. The recorded voltages can be used to predict the voltages of cells made from combinations of the beakers.

#### **Materials:**

100 ml 1.0 M zinc nitrate,  $\text{Zn}(\text{NO}_3)_2$  (To prepare 100 mL of solution, dissolve 30 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 60 mL of distilled water and dilute the resulting to 100 mL)

100 mL 1.0 M copper (II) nitrate,  $\text{Cu}(\text{NO}_3)_2$  (To prepare 100 mL of solution, dissolve 24 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 60 mL of distilled water and dilute the resulting solution to 100 mL)

100 mL 1.0 M lead (II) nitrate,  $\text{Pb}(\text{NO}_3)_2$  (To prepare 100 mL of solution, dissolve 33 g of  $\text{Pb}(\text{NO}_3)_2$  in 60 mL of distilled water and dilute the resulting solution to 100 mL)

ca. 25 mL 1M sodium chloride  $\text{NaCl}$  (To prepare 100 mL of solution, dissolve 5.8 g of  $\text{NaCl}$  in 60 mL of distilled water and dilute the resulting solution to 100 mL)

#### **Large Orange**

25 g sodium sulfide nonahydrate,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$

3 250 ml beakers, with labels

U-shaped drying tube, 10 cm tall

2 cotton balls

Knife to cut orange

10-cm graphite rod, ca 2.5 mm in diameter

zinc metal strip 2 cm × 10 cm × ca 0.8 mm thick

voltmeter that reads 0-2 volts, with clip leads

copper metal strip, 2 cm × 10 cm × ca 0.8 mm thick

lead metal strip, 2 cm × 10 cm × ca 0.8 mm thick

## PROCEDURE

### Preparation:

Label three 250 mL beakers with "1.0M  $\text{Zn}(\text{NO}_3)_2$ ," "1.0M  $\text{Cu}(\text{NO}_3)_2$ " and "1.0M  $\text{Pb}(\text{NO}_3)_2$ ". Pour 100 mL of the appropriate solution into each beaker

Hold the U-shaped drying tube upright and fill it completely with 1M NaCl solutions. Pack a wad of cotton tightly into the opening of each arm of the tube to make a plug about 1 cm long. Invert the tube momentarily to be sure the liquid remains in the tube. If the tube leaks, wad the cotton more tightly.

### Presentation:

Before cutting into the orange, squeeze it repeatedly to break some of its internal membranes and free some of the juice inside the orange. Place the orange on the table and cut two 1-cm holes through its skin. Insert the graphite rod in one hole.

Set the beaker of 1.0M  $\text{Zn}(\text{NO}_3)_2$  next to the orange. Invert the NaCl filled U-tube, and insert one arm in the remaining hole in the orange and the other arm in the beaker of  $\text{Zn}(\text{NO}_3)_2$ . Be sure the cotton plugs in the arms of the U-tube are making contact with the juice in the orange and the solution in the beaker. Insert the zinc strip in the  $\text{Zn}(\text{NO}_3)_2$  solution. Attach the reference (common, black) lead of the voltmeter to the graphite rod in the orange and the positive (red) lead to the zinc strip in the beaker. Record the voltage registered by the meter. (If the voltmeter being used cannot read negative voltages directly, and the reading goes below 0, reverse the leads on the graphite rod and metal strip. Record this reading as negative.)

Repeat the procedure of the previous paragraph with the remaining two beakers of solution and their appropriate metal strips. Record the voltmeter reading for each.

Set the beaker of 1.0M  $\text{Zn}(\text{NO}_3)_2$  beside the beaker of 1.0M  $\text{Pb}(\text{NO}_3)_2$ . Place the zinc strip in the zinc solution and the lead strip in the lead solution. Invert the NaCl filled U-tube, and insert one arm in each beaker. Connect the leads of the voltmeter to the metal strips and record its reading. Repeat this with the other two combinations of metals and solutions (zinc and lead, copper and lead).

## HAZARDS

Lead compounds are harmful when taken internally. The effects of exposure to small concentrations can be cumulative, causing loss of appetite and anemia.

Copper compounds can be toxic if taken internally, and dust from copper compounds can irritate mucous membranes.

## DISPOSAL

The lead nitrate waste should be converted to lead sulfide by adding 25 g of sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) to the solution. The lead sulfide precipitate should be collected and buried in a landfill designed for heavy metals. (Local regulation on the

disposal of hazardous wastes should be consulted) The solution should be flushed down the drain with large volumes of water

The other solutions should be flushed down the drain with water

The leftover orange should not be eaten Discard it in a solid-waste receptacle

## DISCUSSION

The demonstration uses a most unconventional electrode, an orange, as a reference electrode Its unconventionality emphasizes the arbitrary and relative nature of the values of electrode potentials.

The electrode potential of an electrically conductive solid in contact with an electrically conductive solution arises from a difference in electron energy between the bulk of the solid and the bulk of the solution. It is not possible to measure this difference directly The measurement of an electrode potential requires placing another electrically conductive probe in contact with the solution. Another conductive probe in contact with the solution will have its own electrode potential. Therefore, a measurement of energy difference electrodes is actually a measurement of the difference in differences. The energy (potential) of one electrode differs from that of the bulk of the solution by a certain amount, say,  $\Delta E_1 = E_{\text{electrode 1}} - E_{\text{solution}}$  The potential of another electrode differs from the bulk of the solution by another amount,  $\Delta E_2 = E_{\text{electrode 2}} - E_{\text{solution}}$  The measured potential between the two electrodes is  $\Delta E = \Delta E_1 - \Delta E_2$  Thus, all measurements of electrode potentials are, by their nature, relative When an electrode potential is reported, it makes sense only if the electrode used as a reference is also reported

The potential of an electrode depends on both the nature of the solid conductor and the composition of the solution with which it is in contact. Because of this, a reference electrode is usually used with its own standard solution. The solid conductor of the reference electrode is not in contact with the solution containing the electrode whose potential is to be measured. Instead, the reference electrode solution is brought into electrical contact with the solution around the electrode being measured This is accomplished by joining the two solutions with an intermediate solution, a "salt bridge."

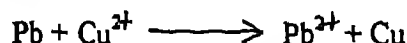
For convenience sake, a small number of reference electrodes have been chosen The fundamental reference electrode is the standard hydrogen electrode This reference is fundamental because its potential has been assigned the value of 0 volts Other reference electrodes are used A common reference electrode is the standard calomel electrode (SCE) This demonstration used an uncommon reference, namely, a graphite rod inserted in an orange

The voltage of each of three metal electrodes in corresponding 1M ion solutions is measured relative to the graphite rod in the orange The measured values correspond to the difference in potential between the orange cell and the metal cells. If the potential of the "standard orange electrode" is assigned a value of 0 volts, then the measured values can be assigned to the metal electrodes. (These metal cell potentials will be called  $E^*$ , the potential relative to the standard orange electrode [SOE]) These  $E^*$  values can be used to predict the measurement that would be obtained if the metal electrodes were to be measured versus each other These predicted values can be compared with the actual measured values to illustrate the utility of the reference electrode.

First, the  $E^*$  values can be tabulated (These are typical values from the demonstration. There is considerable variation among oranges and, therefore, among the SOE potentials)

$E^* (\text{Zn}^{2+}/\text{Zn})$	- 0.90 volt	$\text{Zn}^{2+} + 2 e^- \longrightarrow \text{Zn}$
$E^* (\text{Pb}^{2+}/\text{Pb})$	- 0.50 volt	$\text{Pb}^{2+} + 2 e^- \longrightarrow \text{Pb}$
$E^* (\text{Cu}^{2+}/\text{Cu})$	-0.10 volt	$\text{Cu}^{2+} + 2 e^- \longrightarrow \text{Cu}$

Then, the potential of one metal cell versus another can be calculated. For example, for the cell



The potentials referred to the SOE would give

$$\begin{aligned} E^* (\text{cell}) &= E^* (\text{Cu}^{2+}/\text{Cu}) - E^* (\text{Pb}^{2+}/\text{Pb}) \\ &= (-0.10) - (-0.50) \\ &= 0.40 \text{ volt} \end{aligned}$$

This corresponds to what is found when the cell potential is measured. Since  $E^* (\text{cell})$  is positive, the reaction for the cell would be spontaneous as written.

Because an orange is a complicated and variable mixture of substances, the measurements obtained will vary from orange to orange. However, for a particular orange, there is reasonable correlation between the measured electrode potentials of the metal cells and the published values relative to the standard hydrogen electrode. The measured cell potentials can be converted to values relative to the hydrogen electrode. This is done by taking the difference between one of the measured values, for example, for the  $\text{Cu}^{2+}$ -Cu cell, and the standard value versus the hydrogen electrode, and subtracting this value from the other values measured versus the orange. However, the larger the absolute value of the cell potential, the greater the deviation from accepted values. Thus, the measured potential versus the orange for the zinc cell is likely to be significantly out of line with the standard value.

Precisely what reactions account for the potential of the orange itself are difficult to determine. The juice of an orange contains, in addition to several inorganic salts, quite a few organic substances. Some of these are capable of undergoing electrochemical reactions, for instance, citric acid, ascorbic acid and NADH (nicotinamide adenine dinucleotide hydride). Furthermore, because the orange contains so many substances, the reactions may depend on the potential of the cell connected to it. Cells with higher potentials may cause reactions within the orange that are different from cells with lower potentials. Because of this, the orange does not make a very reproducible cell and is not a good standard cell.

Other fruit can be used in place of the orange. Grapefruits, lemons, limes, tangerines and other citrus fruits are obvious substitutes. As long as the fruit is sufficiently juicy to thoroughly wet the electrode inserted in it, the fruit can serve as a reference cell. Tomatoes can be used; apples are less suitable. Cucumbers may work, and when they're pickled, they certainly will.

## Activity No. 2

### CONSTRUCTING A DRY CELL

Black powder is sprinkled onto a damp felt pad, the pad is wrapped around a carbon rod, and the pad is wrapped, in turn, with zinc foil. When the carbon rod and the zinc foil are connected to the terminals of a battery-operated clock, the clock runs.

### MATERIALS

100 mL-4M ammonium chloride,  $\text{NH}_4\text{Cl}$  (To prepare, dissolve 20 g of  $\text{NH}_4\text{Cl}$  in 85 ml of distilled water )

4 g powdered manganese dioxide,  $\text{MnO}_2$

1 5 volt battery-operated wall clock, without battery

2 20 cm wire leads, 24 gauges, with alligator clips on both ends

Gloves, plastic or rubber

Felt pad 12cm  $\times$  5 cm  $\times$  ca 5 mm thick

15- cm carbon rod, ca 8 mm in diameter (A suitable rod may be obtained from a welding supply shop or recovered by disassembling a discharged 1 5 volt 15- cm  $\times$  6.5- cm diameter dry cell [so called # 6 ignition battery] )

zinc metal foil, 12 cm  $\times$  12 cm  $\times$  ca. 0 25 mm thick

ca 30 cm string

voltmeter, with probes

### PROCEDURE

#### Preparation:

Clip one lead to each of the battery terminals of the battery operated wall clock.

#### Presentation:

Wearing gloves, moisten the felt pad by immersing it in the saturated  $\text{NH}_4\text{Cl}$  solution and squeezing it. Sprinkle 4 g of  $\text{MnO}_2$  in a layer onto the pad. Wrap the pad around the carbon rod with the  $\text{MnO}_2$  between the carbon and the pad. Wrap the zinc foil tightly around the pad, making sure the zinc does not touch the carbon rod (fig - 1). Tie the assembly together with string. Press one of the probes of the voltmeter against the zinc and the other probe against the carbon rod. Record the voltage. Attach the lead from the positive terminal of the wall clock to the carbon rod, and clip the other lead to the zinc foil. The clock will start and run for at least half an hour.

## HAZARDS

Manganese dioxide is a strong oxidizing agent. The felt pad should not be allowed to dry out in contact with manganese dioxide.

Ammonium chloride is toxic when taken internally.

## DISPOSAL

The zinc foil can be rinsed, air-dried and reused in repeated presentations of the demonstration until it becomes too corroded to bend without breaking. It should then be discarded in a solid-waste receptacle.

The felt pad should be rinsed under running water to remove the manganese dioxide and ammonium chloride. It can be air dried for reuse or discarded in a solid waste receptacle.

The ammonium chloride solution should be flushed down the drain with water.

## DISCUSSION

In this demonstration, a dry cell is constructed from a carbon rod surrounded by manganese dioxide, which is wrapped in turn with a pad moistened with ammonium chloride solution and then with a zinc strip. The zinc and carbon electrodes are at different potentials. Initially, the cell produces about 1.5 volts, and electrons flow through the external circuit from the zinc to the carbon. The reaction that produces electrons is the oxidation of zinc metal.



At the carbon cathode manganese dioxide is reduced.

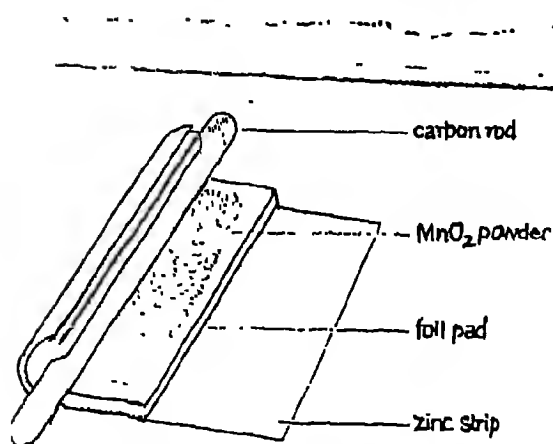
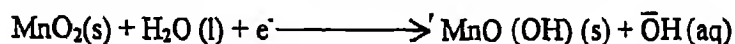


Figure 1. Assembly of dry cell

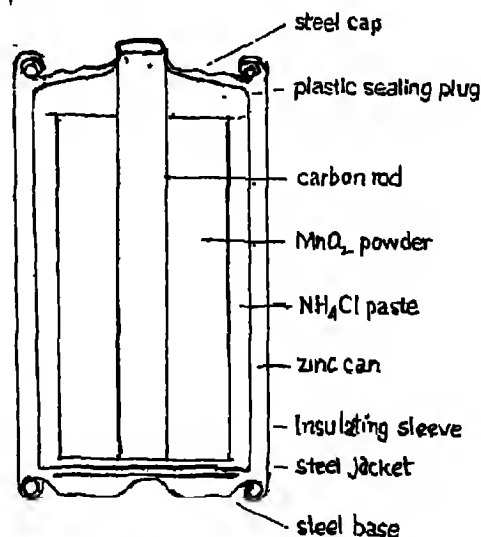


Figure 2. Commercial dry cell



## **GRADING IN SCHOOLS**

### **GRADING IN SCIENCE AND MATHEMATICS**

#### **Introduction:**

1. Evaluation is an integral part of the teaching – learning process
2. Evaluation is a process of collecting, analysing and interpreting evidences of student's learning for making variety of decisions.
3. While assessing students' achievement, we need to focus on students' progress with reference to:
  - Self
  - Peer group
  - Criteria set by the teacher

#### **WHAT IS GRADING**

1. The word 'grade' is derived from the Latin word 'gradus' where it means 'step'.
2. Grading is a process in which students may be classified into groups on the basis of their performance.
3. Grading is a device of recording and reporting student's performance.

#### **FUNCTIONS OF GRADING**

1. It gives an account of the extent to which the instructional objectives have been realised by the learner.

- 2 It helps in making decisions pertaining to placement, promotions and awarding scholarship
- 3 It helps in reviewing transactional strategies and curricular appropriateness

## **LIMITATIONS OF MARKING SYSTEM**

- 1 Currently students' achievement is being carried out only in scholastic areas by awarding marks on a 101-point scale that runs from 0-100
  - a Where zero is not absolute zero. It does not represent nothingness of an attribute,
  - b. Where 100 is not the absolute 100. It does not represent mastery level in the subject.
2. The scale so used suffers from number of limitations, like the arbitrary nature of both the zero and the hundred, imperfection of tools, inter & intra examiner variability etc.
3. As a consequence of these limitations, the marks so awarded do not represent the true mark because of inherent errors of measurement.
4. A random sample of size 'n' is drawn from a population, whose mean is  $\mu$  and standard deviation is  $\sigma$  (which are unknown) Let the mean and standard deviation of the sample are 50 and 10, then the mean of population may lie in between
  - a 40 and 60 in 68 % of cases;
  - b 30 and 70 in 95 % of cases,
  - c 20 and 80 in 99 % of cases

- 5 The negative effect of pass/fail system is going to be glaring day-by-day. A child failed once in examination is labelled as failed through out his life. As a result, the students are forced to even commit suicide.
- 6 Inter- and intra-examiner variability in the marking of the script is so high that it decreases reliability of the scores.
- 7 Marking system has increased cutthroat competition among the students leading to use of unfair means.
- 8 Over emphasis on marks has made the present evaluation system inhumane,
- 9 Comparison of student's performance in various subjects on the basis of raw marks is irrational, unjustifiable and inhumane.
10. The system of pass/fail encourages commercialization of education.
11. In pass/fail system there is a colossal wastage of humane resources at the national level.
12. In marking system there is no provision for improving performance by the students if he/she is not satisfied.

### **ADVANTAGES OF GRADING SYSTEM**

1. The shortcomings of marking system can be overcome to a large extent if students are placed in ability bands that represent ranges of scores. Each ability range may be designated with a letter called a "Grade".
2. Grades can fruitfully be used for recording the growth and development of individual students.

3. Grades can be added meaningfully without distorting the scale of measurement, should we decide to arrive at the Grade Point Average (GP A).
4. Undue significance attached to raw scores will be considerably reduced
5. Grades will be minimally affected by test-difficulty. —————
6. Negative effect of pass/fail will be eliminated, as the performance of individual student will be rated in terms of grades. No grade signifies the failure of student in a subject rather it provides an opportunity to improve on it.
7. Grades so awarded will indicate the relative position of the individual student vis-a-vis his/her group and thus serve the purpose of norm reference testing
8. Grades will provide for comparability even across the curricular areas because the normal distribution ensures the uniformity in spread of scores regardless of the nature of curricular areas.
9. It may be naive to assume that a shift from marking to grading would remedy entire defects of the conventional system. However grading is far more satisfactory a method.

## **PRE- REQUISITES**

Pre-requisites for any effective examination are:

- Balanced Question Paper,
- Detailed Marking Scheme,
- Randomisation of the Answer Scripts, and
- Fair Conduct of Examination

## **METHODS OF ASSIGNING GRADES**

1. In general, grading may be carried out by two methods
  - a. Direct
  - b. Indirect
2. In direct method, the performance of the students is assessed in qualitative terms and is expressed in terms of letter grades
3. In indirect method, the performance of the students is first assessed in terms of marks and subsequently transformed into letter grades by using different modes.
4. Indirect grading methods may be of two types.
  - a. Absolute grading
  - b. Relative grading
5. Absolute grading warrants direct conversion of marks into grades based on pre-determined standards irrespective of the distribution of marks in a subject. This procedure is simple and straightforward. It should be used in Home Examinations.
6. Relative grading, which is also known as "Grading on the Curve", entails transformation of obtained curve into a desired curve. This conversion allows us to categorize the obtained scores into a number of grades as per our requirement in a scientific manner. It should be used in Public Examinations.

## **ABSOLUTE GRADING IN SCHOLASTIC AREAS**

7. At primary stage, three point scale may be used as given below:

➤ 60% and above	A	Good
➤ 30% - less than 60%	B	Average
➤ Below – 30%	C	Unsatisfactory

8 At Upper Primary stage, five – point scale may be used as given below

➤ 75% and above	A	Excellent
➤ 60% - Less than 75%	B	Very Good
➤ 45 % - Less than 60%	C	Good
➤ 33% - Less than 45%	D	Average
➤ Below – 33%	E	Unsatisfactory

9. In Home Examination at Secondary/Sr. Secondary State, nine – point scale may be used as given below

➤ 90% and above	A	Outstanding
➤ 80% - less than 90%	B	Excellent
➤ 70% - less than 80%	C	Very Good
➤ 60% - less than 70%	D	Good
➤ 50% - less than 60%	E	Average
➤ 40% - less than 50%	F	Average
➤ 30% - less than 40%	G	Below Average
➤ 20% - less than 30%	H	Marginal
➤ Below 20%	I	Unsatisfactory

10. In Public Examinations at Secondary/Sr Secondary stage, relative grading in nine-point scale may be used as given below:

➤ $1.75\sigma$ to $\infty$	4%	A
➤ $1.25\sigma$ to $1.75\sigma$	7%	B
➤ $0.75\sigma$ to $1.25\sigma$	12%	C
➤ $0.25\sigma$ to $0.75\sigma$	17%	D
➤ $-0.25\sigma$ to $0.25\sigma$	20%	E
➤ $-0.75\sigma$ to $-0.25\sigma$	17%	F
➤ $-1.25\sigma$ to $-0.75\sigma$	12%	G
➤ $-1.75\sigma$ to $-1.25\sigma$	7%	H
➤ $-\infty$ to $-1.75\sigma$	4%	I

#### **GRADING IN CO-SCHOLASTIC AREAS**

11. At elementary state, 3-point direct grading may be used,
12. At secondary/Senior Secondary, 5-point direct grading may be used.

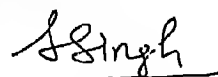
# RECOMMENDATIONS REGARDING USE OF GRADES IN NATIONAL CURRICULUM FRAMEWORK – 2000

Stage	Scholastic	Co-scholastic
Pre Primary	No Formal Teaching & Evaluation	
Primary	3-point Absolute grading	3-point Direct grading
Upper Primary	5-point Absolute grading	3-point Direct grading
Secondary	9-point Absolute grading	5-point Direct grading
Sr Secondary	<ul style="list-style-type: none"> <li>• 9-point Absolute grading in the first 3 semester</li> <li>• 9-point Relative grading in the 4<sup>th</sup> semester examination conducted by the Board.</li> </ul>	5-point Direct grading

## REGIONAL INSTITUTE OF EDUCATION (NCERT) AJMER

List of participants who attended the programme entitled "Training Programme for Teaching Hard-Spots in Higher Secondary Chemistry for Key Resource Persons of Jammu-Kashmir and Haryana states" held at R.I.E., (NCERT) Ajmer from 8<sup>th</sup> –12<sup>th</sup> January, 2004.

S. No.	Name of KRP	Address
1.	Sh. Atulya Joshi	Govt. Sr. Sec. Sachool, Nejadela Kalan, Sirsa, Haryana.
2.	Sh. Jai Singh	Govt. Sr. Sec. School, Chhainsa (Ballabhgarh) Faridabad, Haryana
3.	Sh. Poo <del>ve</del> en Kumar	Govt. Sr. Sec. School, Bakra Market, Ambala Cant, Haryana
4.	Dr. Rajendra Kumar Singh	Govt. Sr. Sec. School, Kund, Rewari, Haryana.
5.	Sh. Sher Singh	Govt. Sr. Sec. School, Fatehabad, Haryana
6.	Sh. Mukhtiar Singh Kadian	Govt. Sr. Sec. School, Jhajjar, Haryana.
7.	Dr. Yog <del>endra</del> Pal Singh	Govt. Sr. Sec. School, Safidion Jind, Haryana
8.	Sh. Deeraj Ahlawat	Govt. Girls Sr. Sec. School, Model Town, Rohtak, Haryana
9.	Mrs. Bindu	SCERT <sup>Hr.</sup> , Gurgaon, Haryana
10.	Mrs. Indu	SCERT <sup>Hr.</sup> , Gurgaon, Hayana
11.	Sh. Ravi Kishore Agnihotri	Govt. Girls Sr. Sec. School, Kirholi, Pehladpur, Sonapat, Haryana
12.	Sh. Bhim Sain	Govt. Girls Sr. Sec. School, Pehowa, Kurukshetra, Haryana



**Dr. Sukhvir Singh**  
(Academic Coordinator)  
Reader in Chemistry



# **REGIONAL INSTITUTE OF EDUCATION, AJMER**

## **ACADEMIC SESSION 2003-04 WORKING PAPER**

**Chemistry Section, DESM,  
RIE (NCERT), Ajmer**

Title of the PAC Programme Training Programme for Teaching Hard spots in Higher Secondary Chemistry for Teachers of J&K and Haryana

Regional Institute of Education, Ajmer one of the constituent units of N C E R T., New Delhi wants to conduct a 5-day programme for +2 Teachers of the states of J&K and Haryana Title of the programme is "Training Programme for Teaching Hard Spots in Higher Secondary Chemistry for Teachers of J&K and Haryana".

School Education is a sector of fundamental importance to both individual and material level processes. With the thrust given to teaching of Science in National Education Policy, attempts have been made by various organisations to reorganize the content and methodologies of school instruction.

NCERT and its constituent units (RIEs) take leading role in developing curricular materials for teaching science at all the levels of school education **National Curriculum Framework for School Education - 2000**, developed by NCERT gives challenging opportunities for quality work in Science subjects at Senior Secondary Level

As per the guidelines provided in the National Curriculum Framework for school Education - 2000, it is known that new books have been written by the N C E R T at +2 level In pursuit of this first edition of A Textbook for class XII in chemistry was published in March, 2003 by the N C E R T By now it is hoped that teachers must have gone through this book in detail It would be naïve to say that several new concepts in chemistry have been included In the lime – light of these new concepts it is felt that some of these concepts may be rather difficult to transact to the Senior Secondary learners of the School

Department of Education in Science and Mathematics (DESM) one of the departments of RIE, Ajmer has decided to take up this programme with the following objectives in mind

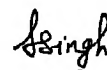
- a) To identify difficult topics from the Text Book
- b) To provide enrichment material on the identified topics
- c) To perform newly included activities/practicals

Keeping the above objectives into consideration the following methodology is adopted

- i) With the help of NCERT Text Book in Chemistry for Class XII, Hard Spots will be identified by the Internal faculty members of Chemistry Section of DESM, RIE, Ajmer
- ii) Concept centered enrichment material is prepared on these Hard spots by the Internal faculty members

Some of the Hard spots that will be discussed during the workshop are  
i) Effective Nuclear charge and its calculation ii) Calculation of crystal Field Stabilization Energy in the complexes iii) Binodal curve for magnetic property of Lanthanides iv) Electrochemistry v) Alkyl/Aryl Halides in organic chemistry.

After completion of in house activities, a Training programme is planned for five day duration. In the Training part discussion on the above Hard spots would be taken up Besides this some new experiments/activities would be tried out in the Chemistry Laboratory It is hoped that observations of the activities/experiments would be recorded by the participating Teachers individually



**Dr. Sukhvir Singh**  
(Academic Coordinator)  
Reader in Chemistry,  
RIE, Ajmer

## TIME SCHEDULE

### DESM, RIE, AJMER

**Title of the Programme: Training Programme for Teaching Hard Spots in Higher Secondary Chemistry for Teachers of J&K and Haryana.**

**Duration: Five days**

**From: 8- 12 January, 2004**

**Venue: RIE, Ajmer.**

Date & Day	Time	Particulars of the Activity
8 1 2004 <b>Thursday</b>	9 00 am to 1 00 pm	Registration of the participants and discussion on Working Paper
	2 00 pm to 5 30 pm	Discussion on Hard Spots of Inorganic Chemistry by Dr S S
9 1 2004 <b>Friday</b>	9 00 am to 11 00 am	Discussion on some topics of Organic Chemistry at Sr Sec Level by Dr R K Parashar
	11 00 am to 1 00 pm	Discussion on some topics of Physical Chemistry at Sr Sec Level by Mrs R V
	2 00 pm to 5 30 pm	With the help of NCERT Text Books of Chemistry (Class XI and XII) activities are to be sorted out by the participants which can be done in the class room
10 1 2004 <b>Saturday</b>	9 00 am to 11 00 am	Discussion on need based concepts of Organic Chemistry at Sr Sec Level by Dr R K P
	11 00 am to 1 00 pm	Discussion on need based concepts of Physical Chemistry at Sr Sec Level by Miss V J
	2 00 pm to 5 30 pm	Try out of the Activities by the participants individually sorted out earlier
11 1 2004 <b>Sunday</b>	9 00 am to 1.00 pm	Innovative experiment/theory and procedure
	2 00 pm to 5 30 pm	Observations, calculations and Result of the exp
12 1 2004 <b>Monday</b>	9 00 am to 1 00 pm	Evaluation Techniques by Dr S C B
	2 00 pm to 5 30 pm	Presentation of Selective Hard Spot topic in Phy/Org /Inorganic Chemistry by the participants Finalization of report and Payment of TA/DA.

#### RESOURCE FACULTY

1. Dr. S. C. Bhargava I/C Chemistry (SCB)
2. Dr. Sukhvir Singh (SS)
3. Dr. R. K. Prashar (RKP)
4. Mrs. Ruchi Verma (RV)